Kinetic Modelling of Cyclohexane Oxidation with the PAH Precursor Formation

A thesis accepted by the Faculty of Aerospace Engineering and Geodesy of the University of Stuttgart in partial fulfilment of the requirements for the degree of Doctor of Engineering Sciences (Dr.-Ing.)

by

Mehdi Abbasi

born in Rasht, Iran

Main referee: Prof. Dr. rer. nat. Uwe Riedel
Co-referee: Prof. Dr.-Ing. Oskar J. Haidn

Date of defence: 31.10.2019

Institute of Combustion Technology for Aerospace Engineering (IVLR)
University of Stuttgart
2019

Acknowledgement

Foremost, I would like to express my sincere gratitude to my advisor Dr. Nadeshda A. Slavinskaya, whose continuous support has been vital for this research. I would also appreciate her for her sense of patience, motivation, and enthusiasm.

Besides, I would like to thank Dr. Elke Goos, for her efforts and supports, in the way of compilation of this manuscript.

Last but not the least, I would like to thank my dear parents and close friends for their spiritual supports alongside this way.

Abstract

A semi-detailed reaction mechanism of cyclohexane (cyC_6H_{12}) has been developed to study cyclohexane oxidation at both low and high temperatures, including the Polycyclic Aromatic Hydrocarbons (PAH) precursor formation routes. This is a significant update of the earlier developed models, as a part of a larger framework, with the aim to develop an optimal surrogate model for kerosene, at the German Aerospace Centre (DLR), Institute of Combustion Technology (VT). The new cyC_6H_{12} model is based on the most recent studies of C_0-C_3 chemistry and includes a PAH sub-model, which contains the molecules with up to five aromatic rings. Improvements have been achieved through revising main reaction classes, evaluating uncertainty boundaries of reaction rate coefficients, and through extension of the low temperature oxidation kinetics by new pathways, especially the cyclohexenyl peroxy formation and the isomerization of cyclic hydroperoxy peroxy hydrocarbon radicals. For the main reaction classes, the uncertainty margins of the rate coefficients have been evaluated.

The calculation of thermodynamic data, such as standard formation enthalpy, entropy, and heat capacity, for key species relevant to the combustion of cyclohexane has been performed by applying the Benson Group Additivity method. The properties of 17 new Benson groups, and 8 ring correction factors for cyclic species were estimated through different empirical and semi-empirical methods. The calculation methods and properties of the estimated groups have been validated by comparing with literature data for the well-studied species and for cyclohexane decomposition products appearing in other cyclohexane kinetic models. The obtained properties were given in the form of NASA polynomial coefficients. The main required terms for transport properties of the intermediates have been studied and calculated using additivity rules and structural similarity approaches.

The cyclohexane mechanism was successfully optimized and validated against ignition delay data from rapid compression machines (RCM) and shock tube (ST) experiments, laminar flame speed data, and species concentration profiles of burner stabilized flames. The developed model reproduced realistic combustion behaviour in all tested conditions and can be used for cyC_6H_{12} oxidation studies. Existence of the negative temperature coefficient (NTC) region in cyC_6H_{12} oxidation has also been investigated. It was found that, a clear NTC behaviour, which was observed in the RCM experiments, could not be obtained in the simulations with the current model. However a general agreement with data from the RCM experiments has been achieved. This is also in agreement with the other ST measurements, where no NTC region was detected at low temperature. The simulations performed with other published models, revealed that they were unable to accurately reproduce the ST data, although they could well describe the NTC region of RCM data. It was also shown that, the cyC_6H_{12} oxidation chemistry is controlled by competition between three main reaction pathways over the full temperature interval. Instead of the NTC behaviour, the dependence of the cyC_6H_{12} ignition on the temperature has a region of a gradient change (RGC), a gradual passage between two different competing reaction schemes of the overall reactivity, which occurs in the temperature range of 800 K < T < 1100 K.

The developed model successfully describes laminar flame speed data and species profiles from burner stabilized, premixed flames. It should be noted that for T < 1600 K, the main reaction route towards the aromatics formation is the cascading dehydrogenation of cyC_6H_{12}. At higher temperatures, this process is mostly controlled by the propargyl radical recombination.

Kurzfassung

Ein semi-detaillierter Reaktionsmechanismus für Cyclohexan (cyC_6H_{12}) wurde entwickelt, um die Oxidation von cyC_6H_{12} bei hohen- und niedrigen Temperaturen, einschließlich der Bildung von polyzyklischen aromatischen Kohlenwasserstoffen (PAK) zu untersuchen. Dies ist eine beachtliche Aktualisierung früher entwickelter Modelle, mit dem Ziel ein optimales Surrogat-Modell für Kerosin zu entwickeln, die ein Teil eines großen Forschungsbereichs im Institut für Verbrennungstechnik (VT) des Deutschen Zentrums für Luft- und Raumfahrt e. V. (DLR) sind. Das neue Cyclohexanmodell basiert auf den neusten Forschungen im Bereich der C_0-C_3 Kinetik und schließt ein PAK-Teilmodell ein, das Moleküle mit bis zu fünf aromatischen Ringen beinhaltet. Verbesserungen wurden durch eine Überarbeitung der Hauptreaktionsklassen, Bewertung der Unsicherheitsgrenzen der Reaktionsgeschwindigkeitskoeffizienten und durch eine Erweiterung der Niedertemperaturoxidationskinetik durch neue Reaktionspfade, insbesondere der Cyclohexenylperoxybildung und der Isomerisierung der zyklischen Hydroperoxy-Peroxykohlenwasserstoffradikale, erreicht. Für die Hauptreaktionsklassen wurden die Unsicherheitsgrenzen der Geschwindigkeitskoeffizienten bewertet.

Die Berechnungen der thermodynamischen Eigenschaften, wie Standardbildungsenthalpie, Entropie und Wärmekapazität für die Hauptspezies der Verbrennung von Cyclohexan wurden mit der Benson Gruppenadditivitätsmethode durchgeführt. Die Eigenschaften von 17 neuen Benson-Gruppen und 8 Ringkorrekturfaktoren für zyklische Substanzen wurden durch verschiedene empirische und halbempirische Methoden abgeschätzt. Die Berechnungsmethoden und die Eigenschaften der neu abgeschätzten Gruppen wurden durch Vergleich mit Literaturdaten für gut untersuchte Substanzen und für Cyclohexanzerfallsprodukte, die auch in anderen Cyclohexanreaktionsmechanismen vorkommen, validiert. Die erhaltenen Eigenschaften wurden im NASA-Polynom Format angegeben. Die wichtigsten Parameter der Transporteigenschaften der Zwischenprodukte wurden untersucht und durch Anwendung von Additivitätsregeln und Strukturähnlichkeitsansätzen berechnet.

Der Cyclohexanmechanismus wurde an Zündverzugszeitdaten einer Rapid Compression Machine (RCM) und von Stoßrohrexperimenten (ST), an laminaren Flammengeschwindigkeitsdaten, sowie Konzentrationsprofilen von brennerstabilisierten Flammen erfolgreich optimiert und validiert. Das entwickelte Modell reproduziert realistisches Verbrennungsverhalten in allen getesteten Bedingungen und kann für Cyclohexanoxidationsstudien benutzt werden. Die Existenz des Bereichs mit negativen Temperaturkoeffizienten (NTC) in der Cyclohexan (cyC_6H_{12}) Oxidation wurde ebenfalls untersucht. Ein deutliches NTC-Verhalten, das in RCM Experimenten beobachtet wurde, konnte durch Simulationen mit dem jetzigen Modell nicht erhalten werden. Jedoch wurde eine generelle Übereinstimmung mit den Daten der RCM Experimente erreicht. Das ist auch in Übereinstimmung mit anderen ST-Messungen, bei denen auch keine NTC-Zone bei niedrigen Temperaturen beobachtet wurde. Die durchgeführten Simulationen mit anderen bereits veröffentlichten Modellen verdeutlichen, dass sie nicht in der Lage waren die ST-Daten genau zu reproduzieren, obwohl sie die NTC-Zone von RCM Daten gut beschreiben können. Es wurde auch gezeigt, dass über das gesamte Temperaturintervall die cyC_6H_{12} Oxidationschemie durch die Konkurrenz zwischen drei Hauptreaktionspfaden kontrolliert wird. Anstatt eines NTC-Verhalten, hat die Temperaturabhängigkeit der Zündung von Cyclohexan einen Bereich mit allmählichen Änderungen (RGC), d.h. einen schrittweisen

Übergang zwischen zwei verschiedenen konkurrierenden Reaktionsschemata der Gesamtreaktivität, der in einem Temperaturbereich von 800 K < T < 1100 K stattfindet.

Das entwickelte Modell beschreibt ebenfalls erfolgreich die laminaren Flammengeschwindigkeitsdaten, sowie Speziesprofile aus stabilisierten vorgemischten Flammen. Es sollte auch angemerkt werden, dass bei T < 1600 K, die sequenzielle Dehydrierung (Cascade Dehydrogenation) von Cyclohexan der Hauptreaktionspfad für die Bildung der Aromaten ist. Bei höheren Temperaturen wird dieser Verlauf hauptsächlich durch Rekombination von Propargylradikalen kontrolliert.

Table of Contents

List of Tables

List of Figures

Nomenclature

Roman letters	
A	Pre-exponential factor
c	Speed of light
$C_p(T)$	Heat capacity
$C_{p,rot}$	Rotational heat capacity contribution
$C_{p,tran}$	Translational heat capacity contribution
$C_{p,vib}$	Vibrational heat capacity contribution
E_a	Activation energy
$f_l(T)$	Lower reaction rate constant uncertainty boundaries
f_s	Correction factor for pre-exponential factor
$f_u(T)$	Upper reaction rate constant uncertainty boundaries
I	Net 3D moment of inertia around the centre of mass
I_m	Total internal axial moment of inertia
I_x	Moment of inertia around the *x*-axis
I_y	Moment of inertia around the *y*-axis
I_z	Moment of inertia around the *z*-axis
k_0, k_{opt}	Average reaction rate constant
k_b	Boltzmann's constant
k_{low}	Lower reaction rate constant
k_{upper}	Upper reaction rate constant
M	Molecular weight
m	Number of literature kinetic datasets
M_{model}	Molecular weight of model molecule
M_{target}	Molecular weight of target molecule
m_x, m_y	Molecular weight of the collision partners x, y
n	Number of modified parameters in the FUMILI goal function
n_0	Last modified parameter
N_A	Avogadro's number
n_A	Number of atoms in a molecule
P	Pressure
P_c	Critical pressure
P_{vp}	Vapour pressure
R	Gas constant
R_0	Collision diameter
r_d	Separation distance
$s(x)$	Error for each modified parameter

S^0	Standard entropy
S_l	Laminar flame speed
S_{rot}	Rotational entropy contribution
S_{tran}	Translational entropy contribution
S_{vib}	Vibrational entropy contribution
T	Temperature
t	Time
T_b	Boiling temperature
T_c	Critical temperature
T_r	Dimensionless temperature
$x = hcv/k_bT$	Dimensionless scalar for vibrational frequencies
Z_{rot}	Rotational relaxation collision number

Greek letters

α	Polarizability
β	Exponent of temperature in the reaction rate
ΔH_c^0	Combustion enthalpy
ΔH_f^0	Formation enthalpy
ΔH_r^0	Standard heat of the reaction
ϵ	Magnitude of the electric field
ε	Lennard-Jones well-depth
μ	Dipole moment
μ_m	Reduced mass
σ	Lennard-Jones diameter
σ_e	External symmetry of the molecule
$\varphi(r)$	Lennard-Jones potential
φ	Equivalence ratio
ω	Acentric factor

Abbreviations

C-C	**C**arbon to **C**arbon bond
C-H	**C**arbon to **H**ydrogen bond
C/H	**C**arbon to **H**ydrogen Ratio
CFD	**C**omputational **F**luid **D**ynamics
DF	Difference to literature data
DLR	**D**eutschen Zentrum für **L**uft- und **R**aumfahrt
Exp.	Experiments
GTL	**G**as **t**o **L**iquid
G1-G16	New calculated Benson groups
H	Hydrogen atom
IFS	**I**nput **F**ormula of **S**urrogate
JSR	**J**et **S**tirred **R**eactor
L-J	**L**ennard-**J**ones parameters
MAD	**M**ean **A**bsolute **D**eviation
NASA	**N**ational **A**merican **S**pace **A**gency
NIST	**N**ational **I**nstitute of **S**tandards and **T**echnology

NTC	**N**egative **T**emperature **C**oefficient
OH	Hydroxyl radical/group
HO_2	Hydroperoxy radical/group
OO· , OO	Peroxide group
PAH	**P**olycyclic **A**romatic **H**ydrocarbons
PFR	**P**lug **F**low **R**eactor
pw	**P**resent **W**ork
Q , Q'	Olefins
Q·	Olefin radical
R , R', R·	Alkyl radicals
RCM	**R**apid **C**ompression **M**achine
RGC	**R**egion of **G**radient **C**hange
SOL	**S**urrogate **O**ptimization **L**oop
ST	**S**hock **T**ube
TRO	**T**urbo **R**eact**o**r
TSI	**T**hreshold **S**ooting **I**ndex

1. Introduction

1.1. Introduction to Combustion

Combustion, as a complex thermo-chemical phenomenon, is known as the most important industrial process, with significant effects on different aspects of human life and the environment. This broad field includes many different types of industries, specifically the aviation sector, which has a growing demand for fuels. However, over the last years oil prices have surprised everyone by its historical plunge [1]. Considering that the markets for crude oil, its derivatives, and other fossil fuels, obey several factors and rules, the future access to fossil fuels at a reasonable cost remains uncertain [2]. On the other hand, changes in climate, increasing environmental awareness and instability of fuel costs require improvements in efficiency of energy infrastructure and reduction in pollution [3]. In the last decades, these issues have driven aviation industry to look for alternative fuels or mixtures of crude oil-based kerosene and alternative fuels like GTL (Gas to Liquid), in order to lower fossil fuel dependency and minimize emissions. However, the criterion for alternative fuels, specifically in the aviation sector, such as required atomization, evaporation and burning characteristics, thermal and chemical stability, low viscosity, high lubricity and specific heat capacity are quite restrictive [2]. Despite of many attempts to derive alternative fuels, the commercial crude oil-based fuels remain the main energy sources for technical combustion, particularly in the aviation industry for at least the next decade. Therefore, they remain a focus of scientific investigation.

Commercial fuels normally consist of hundreds of hydrocarbons, which produce a number of intermediates components during combustion. Surrogate style models are normally in use in order to model different blends. In spite of their simplicity, the surrogate model that consists of certain main components, are able to precisely predict the physical and chemical properties. Therefore, the selection of the key surrogate components is the first step in the creation of skeletal kinetic mechanisms for practical fuels like kerosene [3].

1.2. Jet Fuels, Surrogates and Compositions

Various jet blends (kerosene mixtures) are the most widely used fuel mixtures in aviation industry and they are one of the main study cases we focus on due to its widespread usage. Kerosene is defined as a complex mixture of several main hydrocarbons with a length of C_9-C_{18}. They can be categorized into four main families with regards to the molecular structure: n-alkanes (n-paraffins), iso-alkanes (iso-paraffins), cycloalkanes (naphthenes), aromatics, and olefins. The most convenient and widely used kerosene blends are namely Jet A-1, Jet A, JP-8 and JP-5. Among them, the Jet A and Jet A-1 are vastly used as commercial aviation fuels.

Several investigations have also been proposed to identify the composition of kerosene, for instance the study by Gueret et al. [4] who determined that the composition of the fuel TRO consists of 78% of alkanes, 12.2% of aromatics and 9.8% of cycloalkanes. Another example is the investigation performed by Faith et al. [5], which revealed that 99.2% of the detected hydrocarbons from Jet-A blend, are compounds with 9 to 17 carbon atoms, and the compounds

with 12 carbon atoms had the highest presence (19.5%). Table 1.1 summarizes typical kerosene mixtures, their components, and their contribution.

Table 1.1 Composition of different type of kerosene [2].

Kerosene type	Contribution/ % vol			
	Alkane	Cycloalkane	Aromatics	Olefins
TRO	73.9	11.3	14.8	-
Jet-A	37.0	47.0	15.0	1.0
Avtur	51.6	28.7	19.7	<1.0
Avcat	22.7	52.6	24.7	2.0
JP-7	65.0	32.0	3.0	-

It can be understood that, the diverse composition of kerosene and existence of several aliphatic and aromatic compounds makes the kinetic modelling of kerosene and therefore the overall numerical simulation tasks more complicated. This problem can be overcome by applying a surrogate modelling approach. This enhances us with a good representation of real fuels, which can describe physical and chemical properties of the real fuels [3]. Fig 1.1 illustrates the distribution of hydrocarbons in Jet-A due to the main hydrocarbon groups, based on the represented model by the DLR Institute of Combustion Technology [6].

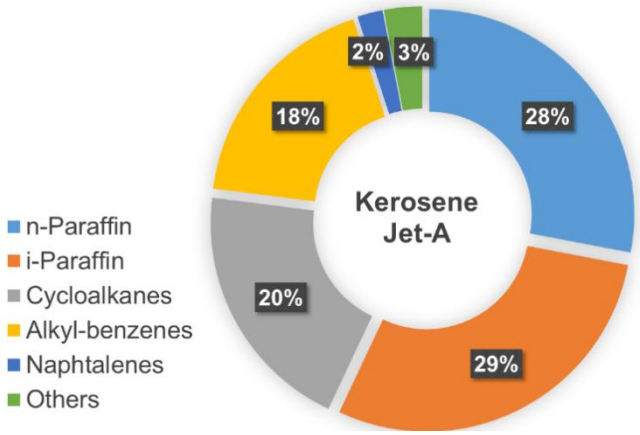


Figure 1.1 Distribution of various hydrocarbon type, used in the kinetic model of kerosene blend Jet-A [6].

A successful surrogate model should be able to satisfy the physical aspects, so that it remains able to consistently simulate the key properties such as density, heat capacity, viscosity, surface tension, and volatility, in addition to meeting the chemical criteria, such as successfully describing the chemical properties, pre-oxidation stability, ignition behaviour, flame speed, and emission behaviour.

Fig 1.2 explains the principle concept of a surrogate model. As illustrated, the first step is the determination of mixture percentages of the present aliphatic groups in the Jet-A blend and the specification of the Input Formula of Surrogate (IFS) for kerosene (Jet-A). This proceeds through validation and optimization of several key physical and chemical parameters and indexes, such as combustion enthalpy, formation enthalpy, molecular weight, C/H ratio, sooting tendency index, critical point, two phase diagram and distillation curve [7]. This is achieved by several iteration steps in the DLR algorithm (Surrogate Optimization Loop (SOL)) developed in [7] to obtain a sufficiently accurate composition of surrogate mixtures. Eventually, the surrogate model must be consistent with experimental results and outcomes of practical combustion devices [2].

The resulting surrogate blend consists of n-propylcyclohexane, iso-octane, dodecane, 1-methylnaphtalene and hexadecane, which represent paraffins, naphthenes and aromatics in the achieved blend [7, 8] (Table 1.2).

The next step in the surrogate model construction is the generation of reaction models for each type of the hydrocarbons present in the model, in order to simulate the fuel heat release, ignition delay times, flame speeds, species concentration, and combustion products formation. In order to avoid complexity in the core model, several mechanism development strategies can be implemented. Using simplifications and analogy rules based on structural and chemical similarities is one of the well-known strategies, which can restrict large intermediate molecules and radicals. This normally proceeds through defining several reaction types and classes in different temperature and pressure conditions. Besides that, lumping of several isomers and equivalent components enables us with simplification of reaction schemes [8]. However, this might have its own problems according to loss of accuracy loss and predictability. Even in the case of a detailed mechanism for large hydrocarbons, the high level of kinetic uncertainty is mainly due to the lack of well-validated thermo-kinetic data.

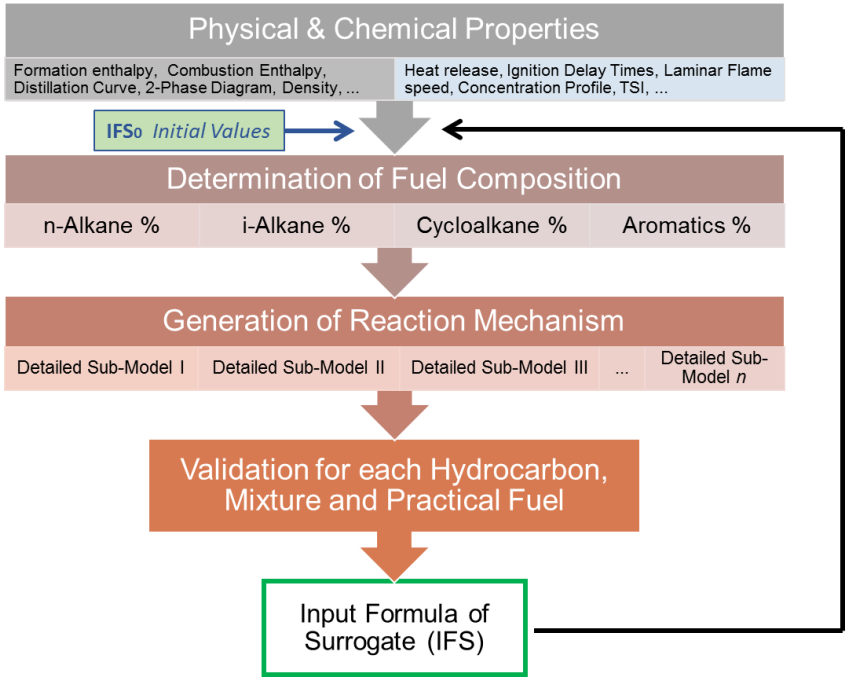


Figure 1.2 The principle scheme for design of the practical fuel reaction model [8].

Table 1.2 Composition of the proposed blend for kerosene combustion and its basic properties [7, 8].

n-propylcyclohexane (C_9H_{18}): 10%	**Combustion enthalpy** $\boldsymbol{\Delta H_c^0}$/ MJ·kg^{-1}	45.0
iso-octane (i-C_8H_{18}): 13%	**Formation enthalpy** $\boldsymbol{\Delta H_f^0}$/ kJ·mol^{-1}	160.0
Dodecane ($C_{12}H_{26}$): 20%	**Molar weight** $\boldsymbol{M_w}$/ g·mol^{-1}	145.0
Methyl-naphtalene ($C_{11}H_{10}$): 25%	**Approximate Chemical formula**	$C_{11}H_{19}$
Hexadecane ($C_{16}H_{34}$): 32%	**Sooting tendency index** ***TSI*** /-	27.8

Therefore, in order to achieve consistent results it is important to build each sub-model based on well-validated core mechanisms for smaller hydrocarbons, and definition of required species and chemical routes [8]. Each of the detailed sub-models in the core model should be separately studied and validated with respect to main kinetic parameters, such as ignition delay time data, laminar flame speed data and concentration profiles.

1.3. Importance of Cycloalkanes (Naphtanes)

Cycloalkanes (naphthenes) are an important chemical class of hydrocarbons found in the composition of kerosene by around 20%. They also own a share of 10% in the Input Formula of Surrogate (IFS) for kerosene (Jet-A) in the DLR Surrogate model, represented by n-propyl cyclohexane (Table 1.2). Besides that, they have a significant presence in the composition of fuels, derived from sand and shale oils. Cycloalkanes can raise soot emission levels due to their cyclic structures. Through dehydrogenation steps, their chemistry can lead to production of aromatics, which can initiate the chain reaction for the production of polycyclic aromatics to soot formation and growth [9].

In spite of their practical relevance, the chemical kinetics of naphthene pyrolysis and oxidation are not intensively investigated as much as n/i-paraffins. Therefore, the kinetic investigation of cyclohexane (cyC_6H_{12}) as the simplest naphthene molecule has a great importance. The reaction models for the first substituted cycloalkanes, such as methyl- and ethyl-cyclohexane, could be developed only based on a validated cyclohexane mechanism. Besides that, among the naphthenes, only cyclohexane is the most experimentally and theoretically studied. For these reasons, the main aim of the current study is to develop a detailed kinetic mechanism for cyclohexane, well-validated on a wide spectrum of experimental data. The kinetic reaction mechanism for cyC_6H_{12} should have a reasonable size in order to study the whole reactivity range, to analyse low and high temperature regimes and the PAH formation, and to be effectively used in various CFD tools. The model is developed, and revised by updating the reaction pathways, as well as the rate coefficients of important reactions with respect to uncertainty quantification assessments, results of the reactions sensitivity analysis, and analysis of rate of production of different species.

The kinetic model is successfully validated against a wide range of experimental data; auto ignition data measured in rapid compression machine (RCM) and shock tube (ST) apparatus, as well as on experimental data obtained from laminar flames (laminar flame speed and species concentration profiles). It is able to provide realistic predictions for cyclohexane combustion and due to its compactness meets the simulation requirements of various CFD tools used for technical combustion system. This model can serve as a basis for possible further extension to substituted, mono- and polycyclic napthenes.

1.4. General Reaction Mechanism Schemes

A similar procedure of sub-model construction can be also assumed for the species larger than C_3. The underlying similarities among the several hydrocarbon types also allow us to apply the same reaction and analogous reaction rate rules for the reactions of the same category [3]. However, depending on the size and structure of hydrocarbons, various types of intermediates, occurs in each sub-model.

Several studies have already been devoted to the detailed modelling of the oxidation of fuels with large hydrocarbon molecules [10-15]. Curran et al. [14, 15] extensively investigated different categories and types of reactions, and developed kinetic models for n-heptane and iso-octane. Their findings and recommendations in [14, 15] are widely used as reference data for the reaction rate coefficients in this reaction model construction. According to their work, two different general schemes of combustion for the low and high temperature regime are recognizable.

1.4.1. High Temperature Scheme

The high temperature scheme is the dominant regime, when the temperature is higher than 900 K. Fig 1.3 explains this general scheme graphically. At higher temperatures the hydrocarbon molecule (C_nH_{2n+2}) decomposes into smaller alkyl radicals, or through losing a C-H bond and producing different isomers of alkyl radicals (C_nH_{2n+1}). This proceeds through a direct unimolecular pathway, or an H-atom abstraction through other active radicals such as O, OH, HO_2, CH_3, C_2H_5, C_2H_3 or O_2.

Through isomerization steps, the radical position can be displaced within the molecule, which enables conversion of one alkyl isomer to another. This is followed by further sequential β-scission of alkyl radicals, which produces smaller alkyl radicals and smaller saturated hydrocarbons. The chain dehydrogenation of C_nH_{2n+1} result in production of the n-olefins (C_nH_{2n}). They also follow the same dehydrogenation (H-atom abstraction) procedure, which results in alkenyl radicals C_nH_{2n-1}, and this trend continues until the complete dissociation.

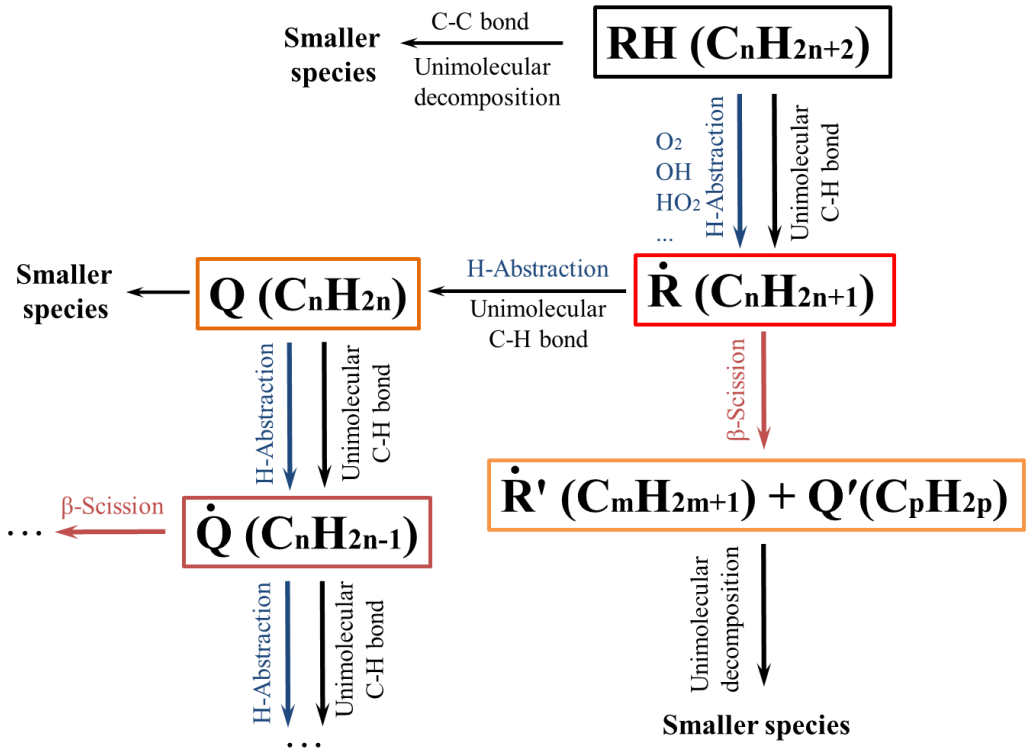


Figure 1.3 The simplified general high temperature oxidation scheme of alkanes [3, 14].

1.4.2. Low Temperature Scheme

Fig 1.4 shows a simplified scheme of the main reaction classes at lower temperature. The low temperature oxidation (T=500-800 K) proceeds through an addition reaction of alkyl radicals with oxygen, which is known as the start reaction for the low temperature [14]. This results in the production of alkylperoxy radicals (ROO˙),(Fig 1.4).

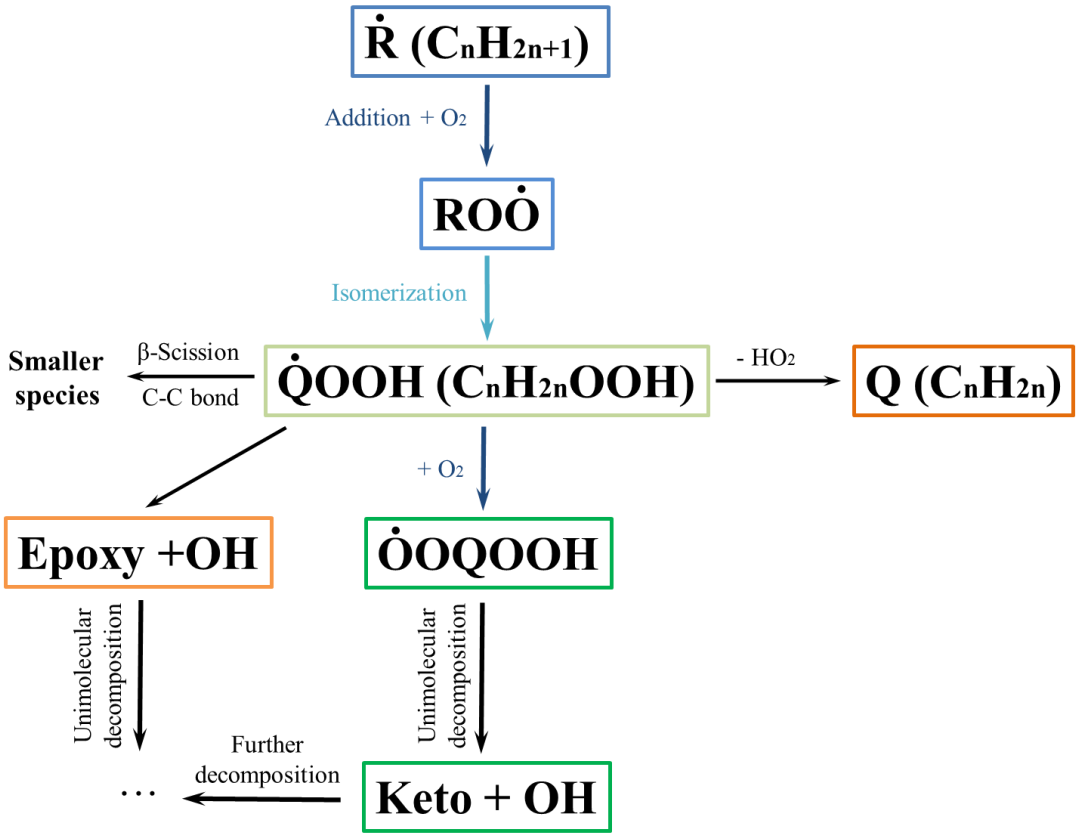


Figure 1.4 The simplified low temperature oxidation scheme of alkanes [3, 14].

The propagation step is a chain reaction, in which hydroxyl radicals (OH) are the main chain carriers [16]. The formation of peroxides is extremely important in this stage. The O-OH bond can be broken into two radicals, which can react with alkane molecules to give alkyl radicals again. An increase in reversibility of the addition reaction (with O_2) by rise in temperature leads to an increase in the formation of alkenes, and decelerates the overall kinetics. This leads to the Negative Temperature Coefficient (NTC) regime, which characterizes a temperature zone, where ignition delay times increase with rising temperature [16].

The oxygen addition step is followed by an internal H-atom abstraction by the peroxy functional group (of the ROO˙ radical) from R, which produces hydro peroxides Q˙OOH. This step is famous as isomerization of ROO˙ and it is one of the key reactions controlling the low temperature oxidation scheme. The resulting hydroperoxyl alkyl radicals (Q˙OOH) decompose into the n-olefins C_nH_{2n} via losing the hydroperoxy group. Alternatively they dissociate to cyclic ethers (epoxies) and a hydroxyl radical, or undergo a β-scission reaction. An addition reaction with O_2 is also predicted for hydroperoxyl alkyl radicals, which leads to formation of ˙OOQOOH.

Through a unimolecular decomposition reaction, the keto hydroperoxides (OROOH) and OH radicals are resulted from ˙OOQOOH. Further molecular decompositions of ketohydroperoxides into smaller species are possible via breaking C-C bonds.

1.5. The Implementation of Smaller Species Chemistry

The kinetic reactions models normally consist of sequential hydrogen and small hydrocarbons sub-models up to larger ones (Fig 1.5). The C_0-C_3 chemistries are in direct interaction with radicals and species such as OH, HO_2, CH, O and O_2, which are important for determination of auto ignition behaviour. They also influence the overall predictions provided by the model. Therefore, it is necessary to enhance the kinetic model with a well-investigated C_0-C_3 chemistry sub-model, in order to accurately describe the main kinetic features, such as flame speed, ignition delay time, as well as species concentration profiles.

The C_0-C_3 kinetic mechanism of current work has been updated through implementation of the most recent kinetic resources, namely syngas and methane mechanisms optimization of Slavinskaya et al. [17, 18] and through data consistency analysis of an acetylene mechanism [19]. For C_4-C_6 chemistries of alkanes, the model benefits from the sub-mechanisms from the Kerosene model of [20].

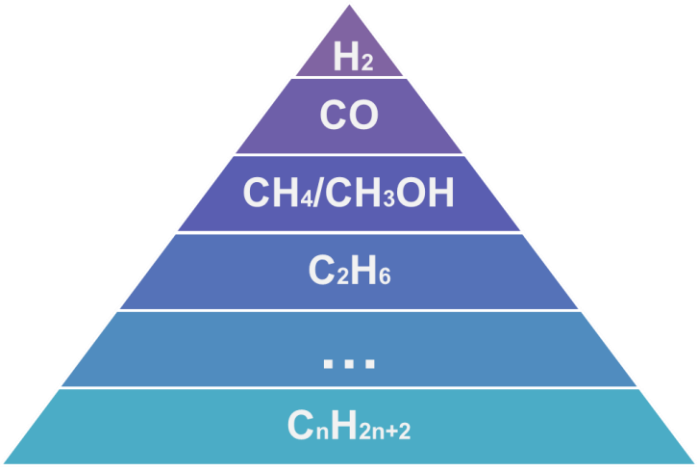


Figure 1.5 Hierarchy of sub-mechanisms within a kinetic reaction mechanism for large hydrocarbons (C_2H_{2n+2}) [21].

2. Development of the Cyclohexane Oxidation Sub-Model

2.1. Review of Existing Cyclohexane Models

In comparison to n-alkanes and iso-alkanes, cycloalkanes have been neither theoretically nor experimentally studied extensively. However, the combustion of cyclohexane (cyC_6H_{12}) has been relatively well-investigated [9, 22-56]. Table 2.1 summarizes the main cyclohexane kinetic models [9, 22-30] investigated in this study to develop the reaction mechanism, the experiments used for validation, and the related experimental set up.

The principal products of the cyclohexane pyrolysis were studied by Tsang [57] in shock tube experiments. Ethylene, 1,3-butadiene, and 1-hexene were identified as the main pyrolysis products. One of the first studies on low temperature chemistry of cyC_6H_{12} oxidation was performed by Zeelenberg and Bruijn [46], who analysed the primary products of the slow oxidation of cyclohexane during the induction period at low temperature and low pressure. Further investigation of the low temperature oxidation with analyses of various reaction paths was undertaken by Klaï and Baronnet [47].

Voisin et al. [22] and Ristori et al. [24] studied experimentally the oxidation of cyclohexane and n-propylcyclohexane, respectively in a jet-stirred reactor (JSR) in the middle-high temperature range and developed high-temperature oxidation sub-mechanisms for cyclohexane. Bakali et al. [23] updated the model of Voisin et al. [22] and validated it on the results obtained in JSR experiment [23] and the flame speed data from Davis [32]. Zhang et al. [26] used the species concentrations from the counter flow flame experiment described in [33, 34] to validate their detailed high temperature combustion scheme. Sirjean et al. [27] investigated experimentally auto ignition of different cyclohexane mixtures in a shock tube (ST) at high temperatures and developed a high-temperature oxidation mechanism.

Granata et al. [25] have proposed a lumped global mechanism for oxidation of cyclohexane both at high and low temperature. They have validated their work against the species concentration profiles from JSR [22, 23] and plug flow reactor (PFR) experiments [44], rapid compression machine (RCM) experiments of Lemaire et al. [31] and laminar flame burning velocity [32]. Silke et al. [9] proposed a detailed mechanism for both low and high temperature, validated versus RCM data of Lille [31] and data from JSR [22, 23]. Buda et al. [29] whose mechanism contains both low and high temperature chemistry also used data from RCM [31] and JSR [22, 23] experiments for validation purposes.

Cavalotti et al. [28] suggested a scheme for low temperature oxidation of cyclohexane based on ab-initio calculations. They validated the model against data from RCM [31] and JSR [22, 23]. Serinyel et al. [30] investigated cyclohexane oxidation at high and low temperature both theoretically and experimentally. Their developed reactions are based on the studies of Sirjean et al. [27, 48, 49]. The new mechanism of Serinyel et al. [30] was successfully validated on a wide spectrum of different experiments, namely concentration profiles from JSR [30], RCM [31, 38]

Table 2.1 Major cyclohexane kinetic mechanisms and their experimental validations (ST: Shock tube, RCM: Rapid Compression Machine, PFR: Plug Flow Reactor, JSR: Jet Stirred Reactor, FL: Flame structure).

Model	Validation				
	ST	**RCM**	**PFR**	**JSR**	**FL**
Voisin et al. [22]				**Concentration profile [22]** **T=** 750-1100 K, **τ** =0.5 s **p=** 10 atm, **φ**=0.5, 1.0, 1.5 **Mixture:** 0.1% $cyC_6H_{12}/O_2/N_2$	
Ristori et al. [24]				**Concentration profile [24]** **T=** 980-1200 K **p=** 1 atm, **φ**=1.0, **τ** =0.07 s **Mixture:** 0.15% $cyC_6H_{12}/O_2/N_2$	
El Bakali et al. [23]				**Concentration profile [23]** **T=** 750-1200 K, **τ** =0.07-0.5 s **p=** 1, 2, 10 atm, **φ**=0.5, 1.0, 1.5 **Mixture:** 0.15% $cyC_6H_{12}/O_2/N_2$	**Flame Speed [32]** **T=** 298 K, **p=** 1 atm **Mixture:** cyC_6H_{12}/ air
Zhang et al. [26]					**Concentration profile [33, 34]** **T=** 1000 K, **p=** 30 Torr **φ**=1.0, 2.0
Sirjean et al. [27]	**Ignition delay time [27]** **T=** 1200-1850 K **p=** 7-9 bar , **φ**=0.5, 1, 2 **Mixture:** 0.5% cyC_6H_{12}/O_2/Ar				
Granata et al. [25]		**Ignition delay time [31]** p_{TDC}= 7-9 bar **T=** 650-900 K **, φ**=1.0 **Mixture:** cyC_6H_{12}/ air	**Concentration profile [44]** **T=** 1155 K, **p=** 1 atm **Mixture (pyrolysis):** 0.166 %cyC_7H_{14} in N_2 **T=** 1160 K, **p=** 1 atm **Mixture:** 0.185% cyC_7H_{14}/1.9% O_2 in N_2	**Concentration profile [22, 23]** **T=** 800-1200 K **p=** 1-10 atm, **φ**=0.5, 1.0, 1.5	**Flame Speed [32]** **T=** 298 K, **p=** 1 atm **Mixture:** cyC_6H_{12}/ air
Silke et al. [9]		**Ignition delay time [31]** p_{TDC}= 7-9, 11-14 bar **T=** 700-1000 K, **φ**=1.0 **Mixture:** cyC_6H_{12}/ air		**Concentration profile [22]** **T=** 850-1070 K **p=** 2.0, 10 atm **φ** = 0.5, 1.0, 1.5, **τ** =0.5 s **Mixture:** 0.1% $cyC_6H_{12}/O_2/N_2$ **Concentration profile [23]** **T=** 800-1100 K, **τ** =0.25 s **p=** 5atm, **φ**= 1.0 **Mixture:** 0.15% $cyC_6H_{12}/O_2/N_2$	
Buda et al. [29]		**Ignition delay time [31]** **p=** 0.7-0.9/ 1.1-1.4 MPa **T=** 700-1000 K, **φ**=1.0 **Mixture :** cyC_6H_{12}/ air		**Concentration profile [22]** **T=** 850-1070 K, **p=** 10atm **φ** = 0.5, 1.0, 1.5 , **τ** =0.5 s **Mixture:** 0.1% $cyC_6H_{12}/O_2/N_2$	
Cavallotti et al. [28]		**Ignition delay time [31]** p_{TDC}= 7-9, 11-14 bar **T=** 700-1000 K, **φ**=1.0 **Mixture:** cyC_6H_{12}/ air		**Concentration profile [23]** **T=** 800-1200 K **p=** 1-10 atm, **φ**=0.5, 1.0, 1.5	
Serinyel et al. [30]	**Ignition delay time** [27] **T=** 1200-1850 K **P=** 7-9 bar, **φ**=0.5, 1, 2 **Mixture :** 0.5% cyC_6H_{12}/O_2 in Ar **Ignition delay time [37]** **T=** 950-1200 K **p=** 13-15 bar, **φ**=0.5, 1.0 **Mixture :** cyC_6H_{12}/ air **Ignition delay time [39]** **T=** 950-1200 K **p=** 1.5,3 bar, **φ**=0.5, 1.0 **Mixture :** cyC_6H_{12}/4%O_2/Ar	**Ignition delay time [31]** p_{TDC}=11-14 bar **T=** 700-1000 K, **φ**=1.0 **Mixture:** cyC_6H_{12}/ air **Ignition delay time [38]** **T=** 600-900K, **φ** = 0.5,1,2 p_{TDC} = 12.5, 20, 40 bar **Mixture:** 2.26% $cyC_6H_{12}/O_2/N_2$		**Concentration profile [30]** **T=** 500-1100 K **p=** 1.07 bar , **τ** = 2 s **φ** = 0.5,1.0,2 **Mixture :** 0.667% $cyC_6H_{12}/O_2/N_2$	**Flame Speed [30]** **T=** 298,358, 398 K **p=** 1 atm, **Mixture:** cyC_6H_{12}/ air **Flame Speed [32]** **T=** 298 K, **p=** 1 atm **Mixture:** cyC_6H_{12}/ air **Flame Speed [35]** **T=** 353 K, **p=** 1 atm **Mixture:** cyC_6H_{12}/ air **Flame Speed [36]** **T=** 353 K **p=** 2, 5, 10 atm **Mixture:** cyC_6H_{12}/ air

and ST ignition delay time data [27, 37, 39], and laminar flame velocity data [30, 32, 35, 36]. Only few of the available theoretical studies are based on direct estimations of rate coefficients of cyclohexane reactions: Cavalotti et al. [28] performed ab-initio calculations at B3LYP/6-31g(d,p) level to identify the states of transient complexes and applied the G2MP2 approach to calculate energy levels of each species related to the low temperature oxidation. Sirjean et al. [48] estimated later reaction rates for unimolecular decomposition steps via ring-opening of cyclohexyl, cyclopropyl, cyclobutyl and cyclopentyl radicals at the CBS-QB3 level of theory. In a later study, Sirjean et al. [49] revised the rate constants for isomerization and some decomposition steps, which were based on the same quantum chemical calculations.

Despite of these extensive modelling investigations on cyclohexane oxidation, the published primary reaction classes and their reference kinetic parameters show significant discrepancies. As it will be later seen (section 2.6.2, Fig 2.6 and Table 2.2), the uncertainty of reaction rate coefficients, for certain reaction classes exceeds even the factor of 10^5. This motivated us to develop a kinetic model for cyclohexane, based on previous studies of the author, Abbasi et al. [55, 54], which is further developed through the following steps:

- Implementation of new C_0-C_3 chemistry;
- Revision of the rate parameters of certain reaction paths at high and low temperature;
- Further model extension for low temperature reaction paths.

2.2. Suggested Scheme for High & Low Temperature Combustion

This mechanism is an improved version of previous models of the author, Abbasi et al. [55, 54], where a kinetic model for cyclohexane was obtained through extension of the high temperature chemistry, specifically cascading dehydrogenation steps, and an initial make of low temperature chemistry [54]. This work was updated in [55], by further extension of low temperature reaction paths and evaluation of the related kinetic data, revision and re-estimation of the thermodynamic and transport properties of intermediates, initial uncertainty investigation of the available kinetic data, and further validation on the newest experimental data. The new model also contains the most recent C_0-C_3 chemistry [17, 19] (also contributed by the author), and a PAH sub-model up to 5-ringed molecules [58, 59]. Similar to the normal saturated alkanes, the reaction mechanism includes two different sub-models for high temperature and low temperature regimes.

2.3. The High Temperature Sub-Mechanism

High temperature oxidation of cyC_6H_{12} evolves via several unimolecular and bi-molecular thermal decomposition routes until formation of aromatics and small species. Fig 2.1 demonstrates this scheme. This will be discussed in detail by explaining different reaction classes in next-coming sections.

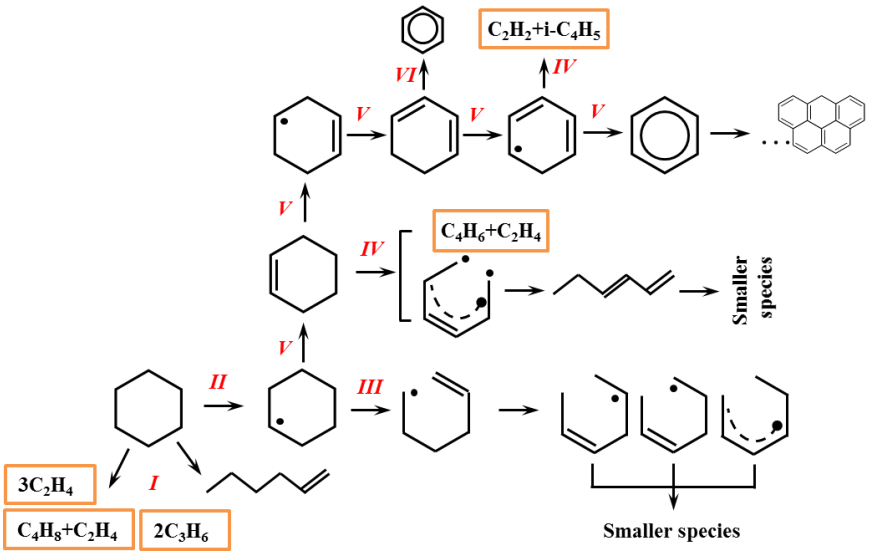


Figure 2.1 Principal scheme of the high temperature oxidation of cyC_6H_{12}. The roman numbers represent various reaction classes.

I. Unimolecular fuel decomposition

Cyclohexane decomposition can be initiated through unimolecular reactions, namely thermal dissociations that proceed through breaking the C-H bond and forming cyclohexyl radicals cyC_6H_{11} (see reaction *R1*), or via ring-opening and the formation of acyclic olefins $a\text{-}C_6H_{12}$ (reaction *R2*) and direct decompositions to smaller species (reactions *R3-R5*):

(R1) $cyC_6H_{12} \leftrightarrows cyC_6H_{11} + H$
(R2) $cyC_6H_{12} \leftrightarrows a\text{-}C_6H_{12}$
(R3) $cyC_6H_{12} \leftrightarrows C_3H_6 + C_3H_6$
(R4) $cyC_6H_{12} \leftrightarrows C_4H_8 + C_2H_4$
(R5) $cyC_6H_{12} \leftrightarrows 3\,C_2H_4$.

II. H-atom abstraction leading to cycloalkyl radical cyC_6H_{11}

In this step, cyclohexane is involved in the series of reactions with smaller radicals such as O, H, OH, HO_2, HCO, CH_3O, CH_3, C_3H_5, vinyl radical (C_2H_3), and O_2, which result in abstraction of H-atom and production of cyclohexyl radical. In spite of importance of this step, the well-known cyclohexane modelling studies used only a reduced reaction set of this type. For example Zhang et al. [26], who investigated the combustion of cyC_6H_{12} at high temperatures, considered this step to be accomplished only with the H, OH, O, CH_3, O_2, and hydroperoxy radicals. The model from Silke et al. [9] does not include abstraction with HCO, CH_3O, and C_3H_5 radicals. Serinyel et al. [30], in updating the reaction model of Buda et al. [29], did not consider the abstractions with O and C_3H_5 radicals. In the current study it has been attempted to include all possible effective reactions in an H-abstraction scheme:

(R6) $cyC_6H_{12} + O_2 \leftrightarrows cyC_6H_{11} + HO_2$
(R7) $cyC_6H_{12} + O \leftrightarrows cyC_6H_{11} + OH$
(R8) $cyC_6H_{12} + H \leftrightarrows cyC_6H_{11} + H_2$
(R9) $cyC_6H_{12} + OH \leftrightarrows cyC_6H_{11} + H_2O$
(R10) $cyC_6H_{12} + HO_2 \leftrightarrows cyC_6H_{11} + H_2O_2$

(R11) $cyC_6H_{12} + HCO \leftrightarrows cyC_6H_{11} + CH_2O$
(R12) $cyC_6H_{12} + CH_3O \leftrightarrows cyC_6H_{11} + CH_3OH$
(R13) $cyC_6H_{12} + CH_3 \leftrightarrows cyC_6H_{11} + CH_4$
(R14) $cyC_6H_{12} + C_2H_3 \leftrightarrows cyC_6H_{11} + C_2H_4$
(R15) $cyC_6H_{12} + C_2H_5 \leftrightarrows cyC_6H_{11} + C_2H_6$
(R16) $cyC_6H_{12} + C_3H_5 \leftrightarrows cyC_6H_{11} + C_3H_6$.

III. Isomerization of cyC_6H_{11}, ring-opening and β-scission reactions

The resulting cyclohexyl radical from the previous stages decomposes further through ring-opening reactions resulting in a linear olefin radical (R17). Another dissociation possibility is breaking the C-H bond and formation of a bi-radical, which quickly converts into a saturated olefin:

(R17) $cyC_6H_{11} \leftrightarrows C_6H_{11}$
(R18) $cyC_6H_{11} \leftrightarrows cyC_6H_{10} + H$.

IV. Direct decomposition of cyclic radicals and unsaturated cyclic molecules

In this step the resulting unsaturated cyclic hydrocarbon is converted into linear forms (in this case C_6H_{10}), or broken into smaller species. The ring-opening step has high activation energy, and therefore is rate limiting. Similar to cyC_6H_{12}, the decomposition via breaking the C-H bond is also considered for cyclohexene, which produces cyC_6H_9 radical:

(R19) $cyC_6H_{10} \leftrightarrows cyC_6H_9 + H$
(R20) $cyC_6H_{10} \leftrightarrows C_6H_{10}$
(R21) $cyC_6H_{10} \leftrightarrows C_4H_6 + C_2H_4$.

V. Cascading dehydrogenation leading to benzene and smaller radicals

Cascading dehydrogenation consists of bimolecular H-atom abstraction (with the help of radical agents as previously described in *type II*) and also unimolecular decomposition through breaking C-H bonds. The series of chain dehydrogenation reactions start from the cyclohexyl radical and as a result, the first cyclic olefin cyC_6H_{10} is produced at this stage. Cyclohexene goes further through similar dehydrogenation steps, resulting in olefin radical (cyC_6H_9). The resulting cyclohexenyl radical also follows the same chain dehydrogenation scheme, and this trend continues until formation of the first aromatic molecule, i.e. benzene (C_6H_6, A1). Therefore, the cascading dehydrogenation is potentially viewed as the decisive chemistry in the high temperature scheme regarding formation of benzene.

In spite of this importance, not all of the cyclohexane kinetic studies have applied all stages of cascading dehydrogenation in their models: the model of Buda [29] does not consider any dehydrogenation further than cyC_6H_{10}, and the later update by Serinyel et al. [30] does not include the complete sets of reactions with the radicals for abstraction of an H-atom. For instance, in the case of H-atom abstraction from cyC_6H_{11} and cyC_6H_9 only the reactions with O_2 were included. The model from Silke et al. [9] contains cascading dehydrogenation paths from cyC_6H_{10} until formation of benzene, but only through unimolecular decomposition of cyclohexene and cyC_6H_8. Meanwhile, only the studies, which focused on high temperature oxidation or pyrolysis of cyclohexane, such as Zhang et al. [26] and Voisin et al. [22], contain

the mentioned pathways up to formation of C_6H_6. The reactions *R22-R32* in *Appendix I* (kinetic mechanism) stand for dehydrogenation of cyC_6H_{11}, *R33-R43* for cyC_6H_{10}, *R45-R55* for cyC_6H_9, *R58-R68* for cyC_6H_8 and *R73-R83* for cyC_6H_7.

VI. cyC_6H_8 reactions toward production of benzene

As also predicted by Orme et al. [60], the two different isomers of cyC_6H_8 (1,3-cyC_6H_8 and 1,4-cyC_6H_8) tend to lose their two hydrogen atoms in order to reach the stable aromatic configuration. This path has been included in the current kinetic model:

$$(R57) \quad cyC_6H_8 \leftrightarrows H_2 + A_1 \quad .$$

Discussing the PAH formation, it also has to be mentioned that a certain number of PAH precursors, such as C_2H_2, C_3H_3, C_3H_4, and C_4H_5 are also generated in the reaction *type IV* by β-scission decomposition of cyC_6H_7 and ring-opening reactions (*R70-R72*).

2.4. The Low Temperature Sub-Mechanism

Oxidation of cycloalkanes at lower temperatures follows the general scheme of acyclic alkanes, and is mainly controlled by addition with O_2, isomerization and decompositions associated with hydroxyl and hydroperoxy radical attack. The low temperature oxidation scheme in the current model is presented in Fig 2.2.

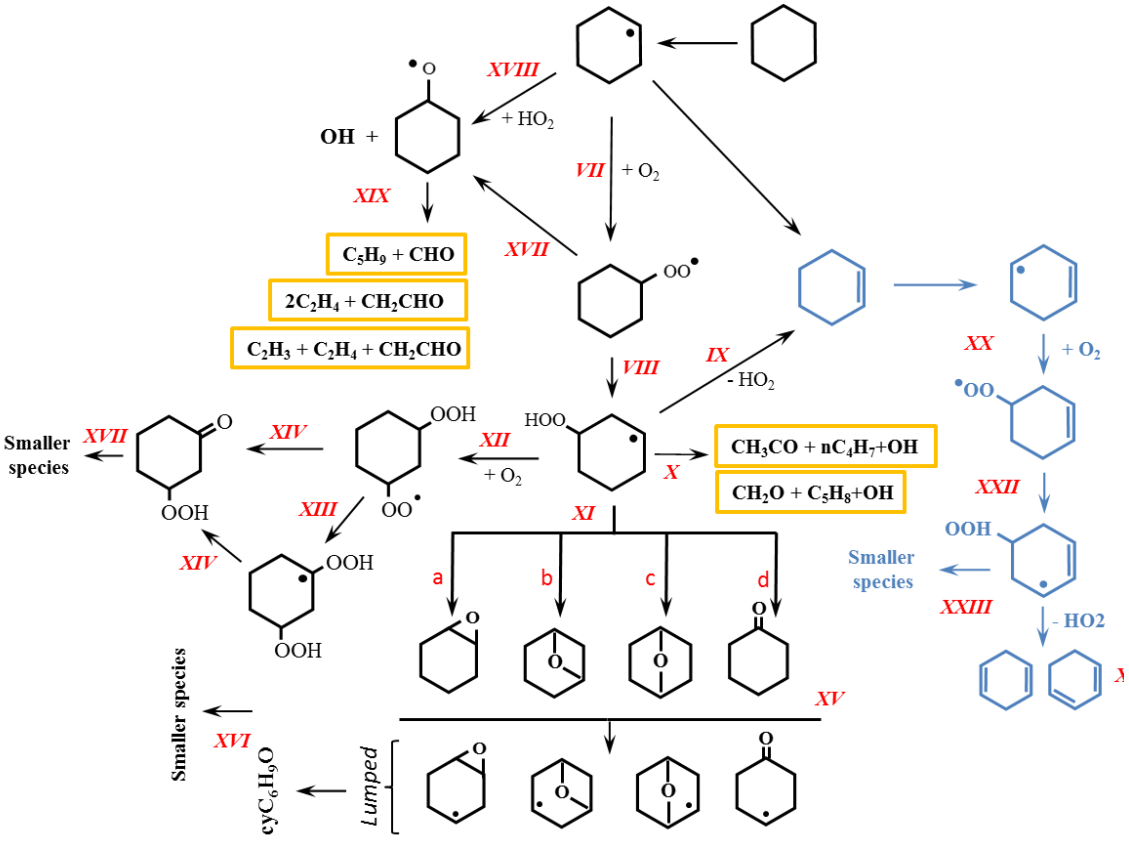


Figure 2.2 Principal scheme of low temperature oxidation of cyC_6H_{12}. The roman numbers represent various reaction classes.

VII. Addition reaction with molecular oxygen

At low temperature, the initiated cyclohexyl radical tends to react with O_2, forming peroxy radicals $cyC_6H_{11}OO\cdot$:

(R84) $cyC_6H_{11} + O_2 \leftrightarrows cyC_6H_{11}OO\cdot$.

This reaction is one of the controlling steps at low temperatures and is particularly important to describe the auto ignition behaviour. For this reaction the rate parameters reported by different models slightly differ from each other. In the proposed mechanism of this work, this is set to the suggested rate of Buda et al. [29], multiplied by a factor of 1.33.

VIII. Isomerization of the cyclic peroxy to the hydroperoxy radical

The isomerization step is about the internal transfer of a hydrogen atom to convert the peroxy into the hydroperoxy functional group [29]. This proceeds through formation of cyclic transition states, with an additional 4-7 members ring [15]:

(R85) $cyC_6H_{11}OO \leftrightarrows cyC_6H_{10}OOH$.

The cyclic structure of cyclohexane enables the build-up of 4 different bi-cyclic transition states, with respect to the location of the peroxy group (see Table 3 of Buda et al. [29]). This results in the creation of 4 different isomers of the cyclic hydroperoxy radical $cyC_6H_{10}OOH$, depending on the locations of the HO_2 group and the position of the C atom. The mechanism of Silke et al. [9] includes reactions of all possible isomers with rate coefficients evaluated by Pitz et al. [61] for methyl-cyclohexane. The mechanism of Buda et al. [29] and its later update [30] contain the four isomers, studied by Sirjean et al. [49] for the isomerization to cycloalkyl hydroperoxy. The low temperature sub-model of Cavallotti et al. [28] considers three different isomers of cyclic hydorperoxy. Also Handford and Wakers [62], who experimentally investigated the kinetics of the H-atom transfer in the cyclohexylperoxy radical, proposed three isomerization paths. In our scheme, similar to the mechanism of Granata et al. [25], four different isomers of the $cyC_6H_{10}OOH$ radical have been lumped into the most stable form, , which was confirmed by investigations of Handford and Wakers [62]. This prevents enlargement of the mechanism, which is important when used in large-scale numerical simulations.

IX. Decomposition of $cyC_6H_{10}OOH$ radicals to cyclohexene and HO_2

The resulting $cyC_6H_{10}OOH$ radical tends to release the hydroperoxy radical, forming cyclohexene *(R86)*:

(R86) $cyC_6H_{10}OOH \leftrightarrows HO_2 + cyC_6H_{10}$.

Silke et al. [9] predicted this path and estimated the backward reaction rate, which is also included in our model.

X. Decomposition of the $cyC_6H_{10}OOH$ radical to smaller species and OH radical

Alternatively, the $cyC_6H_{10}OOH$ radical can decompose into smaller olefins, olefin radicals, aldehydes and the hydroxyl radical via β-scission and ring-opening:

(R87) $cyC_6H_{10}OOH \leftrightarrows CH_3CO + nC_4H_7 + OH$

(R88) $cyC_6H_{10}OOH \leftrightarrows CH_2O + C_5H_8 + OH$.

The rate parameters for these reactions were set analogous to the similar paths within the C_8 sub-model of Ranzi et al. [63].

XI. Decomposition of the $cyC_6H_{10}OOH$ radical and formation of cyclohexanone and bicyclic ethers

Cyclic ethers are the intermediates, produced during low temperature oxidation of alkanes [15]. Depending on the radical position (C·) in QOOH, cyclic ethers can be formed with 3, 4 and 5 ring members. In the current study due to the cyclic structure of the cyclohexane, the bicyclic ether structures are formed (see Fig 2.3, also in Fig 2.2: a,b,c-$cyC_6H_{10}O$):

(R89) $cyC_6H_{10}OOH \leftrightarrows OH + a\text{-}cyC_6H_{10}O$

(R90) $cyC_6H_{10}OOH \leftrightarrows OH + b\text{-}cyC_6H_{10}O$

(R91) $cyC_6H_{10}OOH \leftrightarrows OH + c\text{-}cyC_6H_{10}O$.

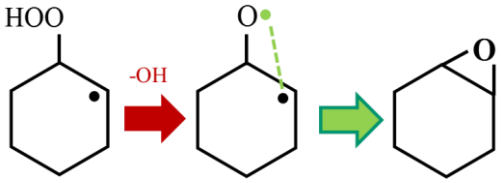


Figure 2.3 Concept of the bicyclic ether formation from hydroperoxy cyclohexyl.

The formation of cyclohexanone (d-$cyC_6H_{10}O$) follows from the same principle. In this case, the HO_2 group and the C· atom take the same position in the structure of QOOH. Disposal of the OH group will result in formation of the carbonyl group, Fig 2.4:

(R92) $cyC_6H_{10}OOH = OH + d\text{-}cyC_6H_{10}O$.

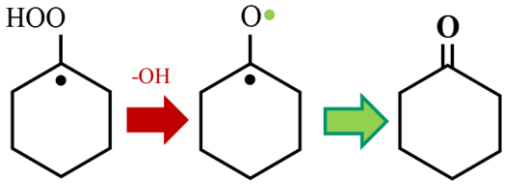


Figure 2.4 Concept of the cyclohexanone formation from hydroperoxy cyclohexyl.

Despite this similarity with the chemistry of the bicyclic ether formation, this reaction is hardly found in other kinetic modelling studies. Sirjean et al. [49] suggested an analogous path for the formation of cyclohexanone from $cyC_6H_{11}OO·$ instead of the $cyC_6H_{10}OOH$ radical. This is interpreted as the decomposition before the isomerization step, which can affect the overall reactivity of the low temperature kinetics. The only model containing this chemistry is the updated model of Serinyel et al. [30]. Their suggested rate coefficients have been implemented in the current mechanism.

XII. Addition of O_2 to $cyC_6H_{10}OOH$ with formation of O_2QOOH

Analogous to the addition step of cyC_6H_{11} with O_2 *(R84)*, the QOOH· radical can also react with O_2 to produce hydroperoxy radical. Similar chemistry for the addition of O_2 to cyC_6H_{11} (reaction *R84*), allows us to assume the same rate coefficients for this reaction:

$$(R93) \quad cyC_6H_{10}OOH + O_2 \leftrightarrows cyOOC_6H_{10}OOH \quad .$$

XIII. Isomerization of $cyO_2C_6H_{10}OOH$ to $cyC_6H_9(OOH)_2$

Due to the presence of the peroxy group within the configuration of $cyO_2C_6H_{10}OOH$, an internal transfer of a H-atom, similar to the isomerization of $cyC_6H_{11}OO$ to $cyC_6H_{10}OOH$, can be considered [36]. According to Curran et al. [15] in the case of acyclic alkanes (particularly the linear C_7 and C_8), this pathway was neglected due to the lack of stability of the resulting radical with two HO_2 groups. However, the ring-strain energy of cyclic species makes it possible to sustain such configurations [9]. This is known as the second stage isomerization, which potentially can improve the model predictions at low temperature:

$$(R94) \quad cyOOC_6H_{10}OOH \leftrightarrows cyOOHC_6H_9OOH \quad .$$

The corresponding rate parameters for these reactions were considered similar to the first isomerization step, *R85*.

XIV. Decomposition of $cyO_2C_6H_{10}OOH$ and $cyC_6H_9(OOH)_2$ to cyclic ketohydroperoxide

Both $cyO_2C_6H_{10}OOH$ and $cyC_6H_9(OOH)_2$ decompose into cyclic ketohydroperoxide and hydroxyl radical, similar to the prediction of Curran et al. [15] for the iso-octane low temperature scheme:

$$(R95) \quad cyOOC_6H_{10}OOH \leftrightarrows cyOC_6H_9OOH + OH$$
$$(R96) \quad cyOOHC_6H_9OOH \leftrightarrows OH + cyOC_6H_9OOH \quad .$$

This proceeds through the internal transfer of a H-atom and formation of C·, accompanied by releasing an OH radical, and stabilization by forming a carbonyl functional group (see Fig 2.5). This takes place after the second stage addition with O_2 (*type XII*) which can produce higher concentration of OH radicals. The rate expressions for *R95* were based on the analogy with i-C_8 recommendations of Curran et al. [15]. For the reaction *R96* the rate rule is considered to be analogous to *R92*, where the $cyC_6H_{10}OOH$ dissociates into cyclohexanone.

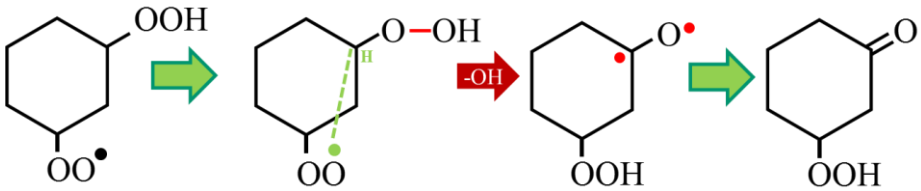


Figure 2.5 Schematic explanation of the O_2QOOH isomerization to carbonyl hydroperoxide.

XV. H-atom abstraction of cyclic ethers and cyclohexanone

Due to the moderate-high temperature condition, once the cyclic ethers formed from the QOOH radical (by reaction *type XI*), they follow the high temperature H-atom abstraction path:

(R97) a-$cyC_6H_{10}O$ + OH ⇆ cyC_6H_9O + H_2O
(R98) a-$cyC_6H_{10}O$ + HO_2 ⇆ cyC_6H_9O + H_2O_2
(R99) a-$cyC_6H_{10}O$ + H ⇆ cyC_6H_9O + H_2
(R100) a-$cyC_6H_{10}O$ + CH_3 ⇆ cyC_6H_9O + CH_4 .

Similar reactions were also found in the models of Serinyel et al. [30] and Silke et al. [9]. This abstraction step follows the reactions with H, OH, HO_2, and CH_3 radicals and results in formation of different isomers of cyC_6H_9O radicals, which are lumped into one in current sub-model (see reactions *R97-R112* in Appendix I).

XVI. Decomposition of cyC_6H_9O radical

Furthermore, the cyC_6H_9O radical decomposes through β-scission, forming acetylene, vinyl radical, i-C_4H_5 radical, and aldehydes:

(R113) cyC_6H_9O ⇆ C_2H_4 + C_2H_4 + HCCO
(R114) cyC_6H_9O ⇆ C_2H_3 + C_2H_4 + CH_2CO
(R115) cyC_6H_9O ⇆ i-C_4H_5 + CH_3CHO .

The reaction rate coefficients for *R113* and *R114* were set as reported by Bogin et al. [64] for cyclohexyl ring opening and for *R115* from Curran et al. [15], there named as *type 18*.

XVII. Decomposition of $OcyC_6H_9OOH$

The cyclic ketohydroperoxide molecule decomposes via ring-opening into smaller oxygenated compounds, such as CH_3CH_2O, CH_2CHO, and CH_2CO (reaction R116, Appendix I):

(R116) $cyOC_6H_9OOH \rightarrow CH_3CH_2O + CH_2CHO + CH_2CO$.

The kinetic parameters for this step were set to the suggestion of Serinyel et al. [30].

XVIII. Formation of $cyC_6H_{11}O$ radical from $cyC_6H_{11}OO\cdot$ and cyC_6H_{11}

The cyclohexyl peroxy $cyC_6H_{11}OO\cdot$ produces via a reaction with CH_3O_2 the alkylproxy radical $cyC_6H_{11}O$, the CH_3O radical, and the O_2 (*R117*). The $cyC_6H_{11}O$ radical is also produced through a homogenous bimolecular decomposition of $cyC_6H_{11}OO\cdot$ (*R118*):

(R117) $cyC_6H_{11}OO$ + CH_3O_2 ⇆ $cyC_6H_{11}O$ + CH_3O+O_2
(R118) 2 $cyC_6H_{11}OO$ ⇆ 2 $cyC_6H_{11}O$ + O_2 .

Alternatively, the $cyC_6H_{11}O$ radical can be formed via the reaction of cyclohexyl with HO_2 radical:

(R119) cyC_6H_{11} + HO_2 ⇆ $cyC_6H_{11}O$ + OH .

The rate parameters for *R117, R118* are set similarly with the existing reaction in C_8H_{18} sub-model, and for *R119*, similar with the same reaction type reaction in C_3H_8 sub-model of Curran et al. [15].

XIX. Decomposition of the $cyC_6H_{11}O$ radical

Decomposition of the alkoxy radical proceeds via ring-opening and yields smaller oxygenated species, such as aldehydes, smaller alkyl and olefin radicals:

(R120) $cyC_6H_{11}O \leftrightarrows C_2H_4 + CH_2CHO + C_2H_4$
(R121) $cyC_6H_{11}O \leftrightarrows C_2H_3 + C_2H_4 + CH_3CHO$
(R122) $cyC_6H_{11}O \leftrightarrows C_5H_9 + CH_2O$.

The rate expressions for *R120* and *R121* were considered interchangeable to the decomposition of $cyC_6H_{10}OH$ in reactions 35 and 36, in Table 2 of Dayma et al. [52]. For reaction *R122*, the kinetic data were set by using the assumption of Curran et al. [15] for reaction *type 18.*

XX. cyC_6H_9 and the formation of cyclohexenyl peroxy $cyC_6H_9OO•$

The additional low-temperature oxidation scheme for cyclic olefins has been added in the current mechanism for the first time, based on the conclusion of Buda et al. [29]. Similar to the cyclohexane scheme, the cyC_6H_9 radical is initiated from cyclohexene. It reacts with O_2 to form cyC_6H_9OO:

(R123) $cyC_6H_9 + O_2 \leftrightarrows cyC_6H_9OO$.

The rate parameters for this reaction were consider similar to the cyclohexane addition step (*type VII*), *R84*.

XXI. Isomerization of cyclohexenyl peroxy to cylohexenyl hydroperoxy cyC_6H_8OOH

The resulting cyC_6H_9OO goes through the (1,5s) isomerization step forming alkenyl hydroperoxy, analogy to cyclohexane:

(R124) $cyC_6H_9OO \leftrightarrows cyC_6H_8OOH$.

XXII. Decomposition of cyC_6H_8OOH to the HO_2 radical and cyclic conjugated isomers 1,3-cyC_6H_8 and 1,4 cyC_6H_8

The alkenyl hydroperoxy decomposes into the HO_2 radical, 1,3-cyC_6H_8 and 1,4-cyC_6H_8, which are lumped together as a cyC_6H_8 molecule:

(R125) $cyC_6H_8OOH \leftrightarrows HO_2 + cyC_6H_8$.

XXIII. Decomposition of cyC_6H_8OOH to OH, aldehydes and smaller conjugated species

The decomposition of cyC_6H_8OOH goes through breaking the C-C bonds, which results in OH, aldehydes and smaller conjugated species:

(R126) $cyC_6H_8OOH \leftrightarrows HCCO + nC_4H_7 + OH$
(R127) $cyC_6H_8OOH \leftrightarrows CH_2O + C_5H_6 + OH$.

The lastly mentioned reactions result in the production of the PAH precursors, namely: cyC_6H_8, C_4H_7 and C_5H_6, which explains the formation of aromatic molecules at temperatures around 900-1000 K (see section 5.2.5.2).

2.5. Empirical Method for the Rate Estimation of Bimolecular Reactions

The kinetics of major H-atom abstraction reactions can be empirically determined. Since this class of reactions is principally bimolecular, the Polanyi-Semenov equations [65] could be used to approximate the activation energy (cal·mol^{-1}) based on the standard heat of the reaction ΔH_r^0:

$$E_a = 48.1 - 0.25|\Delta H_r^0| \quad exothermic\ reaction \qquad Eq\ (2.1)$$
$$E_a = 48.1 + 0.75|\Delta H_r^0| \quad endothermic\ reaction$$

For those reactions with two radicals as reactants, the Polanyi-Semenov equation results in negative values. Therefore, the activation energies are assumed to be negligible.

The pre-exponential factors for cascading dehydrogenation reactions were estimated based on the collision theory of Trautz et al. [66] and Lewis [67]. The calculation method was later completed and proposed by Chernyi et al. [68] as follows:

$$AT^{\beta} = \pi R_0^2 f_s \left[\frac{8k_bT}{\pi\mu_m}\right]^{1/2} N_A \qquad Eq\ (2.2)$$

where R_0 represents the collision radius, k_b is the Boltzmann's constant, T is the temperature, f_s is the correction factor, N_A is the Avogadro's number, and μ is the reduced mass $\mu_m = m_x m_y/(m_x + m_y)$, where x and y are the reactants of a bimolecular reaction. The coefficient f_s is depending on the collision symmetry, for unimolecular homogeneous reactions it is f_s=0.5 and for multi-molecular cases f_s=1.

2.6. Uncertainty Analysis of Literature Data for Reaction Rates

Statistical uncertainty assessments of reaction rates in the present cyclohexane sub-model have been performed based on collected literature data, resulting in the quantification of a feasible region for important reaction types. This feasible range in fact determines the valid boundaries for rate parameter modifications. Besides that, the estimated mean rate values can be viewed as an optimal choice for modification purposes. This proceeds through [19]:

- Review and justification of the main reactions of the cyclohexane oxidation sub-models to update their reaction pool and rate coefficients;
- Evaluation of the uncertainty boundaries (f_u and f_l) of the discussed reaction rates with numerical methods.

The in-house developed tool "REAC-UQ" (partially developed by the author) was used for estimation of mean rates and quantification of uncertainty intervals [19].

2.6.1. Method and Tool Development (FUMILI)

Uncertainty of a reaction model is mainly caused by uncertainty of chemical kinetics data such as reaction rate coefficients, thermodynamic data, transport coefficients data, and also experimental data which is used for validation and model optimization.

The uncertainties of published reaction rates, not only for the chemistry of large hydrocarbons but also smaller species are often not available or rarely reported. In the case of cyclohexane, despite the numerous modelling investigations, the reported rates for certain reactions show significant deviations from each other. Therefore, the uncertainty treatment of the main reaction types within the current sub-model is specifically important for us in order to maintain the accuracy and consistency of the model.

This statistical treatment is based on the non-linear least-squares regression and its numeric realization FUMILI [69, 70, 71], which linearizes the model and approximates the data of "*m*" observations (literature data sets) with a model of "*n*" unknown parameters. However, the statistical assessment of the rate is limited due to the number of available data, where the number of datasets should be larger than the parameters ($m>n$). The evaluation of the parameters is obtained through minimizing an objective function. This scheme was previously implemented for estimation of intermolecular potential parameters and their uncertainties from experimental data of different types. The details of the statistical methodology and the numerical approach, utilized in this scheme are extensively discussed in [19, 71].

Determination of the feasible area follows from the determination of the feasible area of the Arrhenius parameters. The evaluation of the lower and upper rate boundaries follows the approximation of the elements of errors vector for each Arrhenius parameter, i.e., $s(A), s(\beta), s(E_\alpha)$:

$$k_{low}(T) = (A - s(A))T^{(\beta - s(\beta))}exp(-(E_a + s(E_a))/T), \qquad Eq\ (2.3)$$

$$k_{upper}(T) = (A + s(A))T^{(\beta + s(\beta))}exp(-(E_a - s(E_a))/T) \quad .$$

Therefore, the error margin for each reaction included in the model is determined through standard deviations of the rate coefficients *A*, β, E_a and lower and upper uncertainty boundaries f_l, f_u were calculated from the lower and upper reaction rates k_{low}, k_{upper} respectively, and the average (optimum) rate k_0:

$$f_l(T) = \log\left[\frac{k_0(T)}{k_{low}(T)}\right] \quad , \quad f_u(T) = \log\left[\frac{k_{upper}(T)}{k_0(T)}\right] \qquad Eq\ (2.4)$$

2.6.2. Assessment of Available Literature Data

Quantification of the uncertainty intervals was performed over the temperature range of 500-3000 K and for all 3 parameters in the Arrhenius equation. The uncertainty analysis has been done, only if a minimum number of datasets (i.e. in this case at least 3 sets) were available for reaction rate coefficient. If the uncertainties of kinetic data were reported by the references, they have also been taken into account and assigned as the weights of observations.

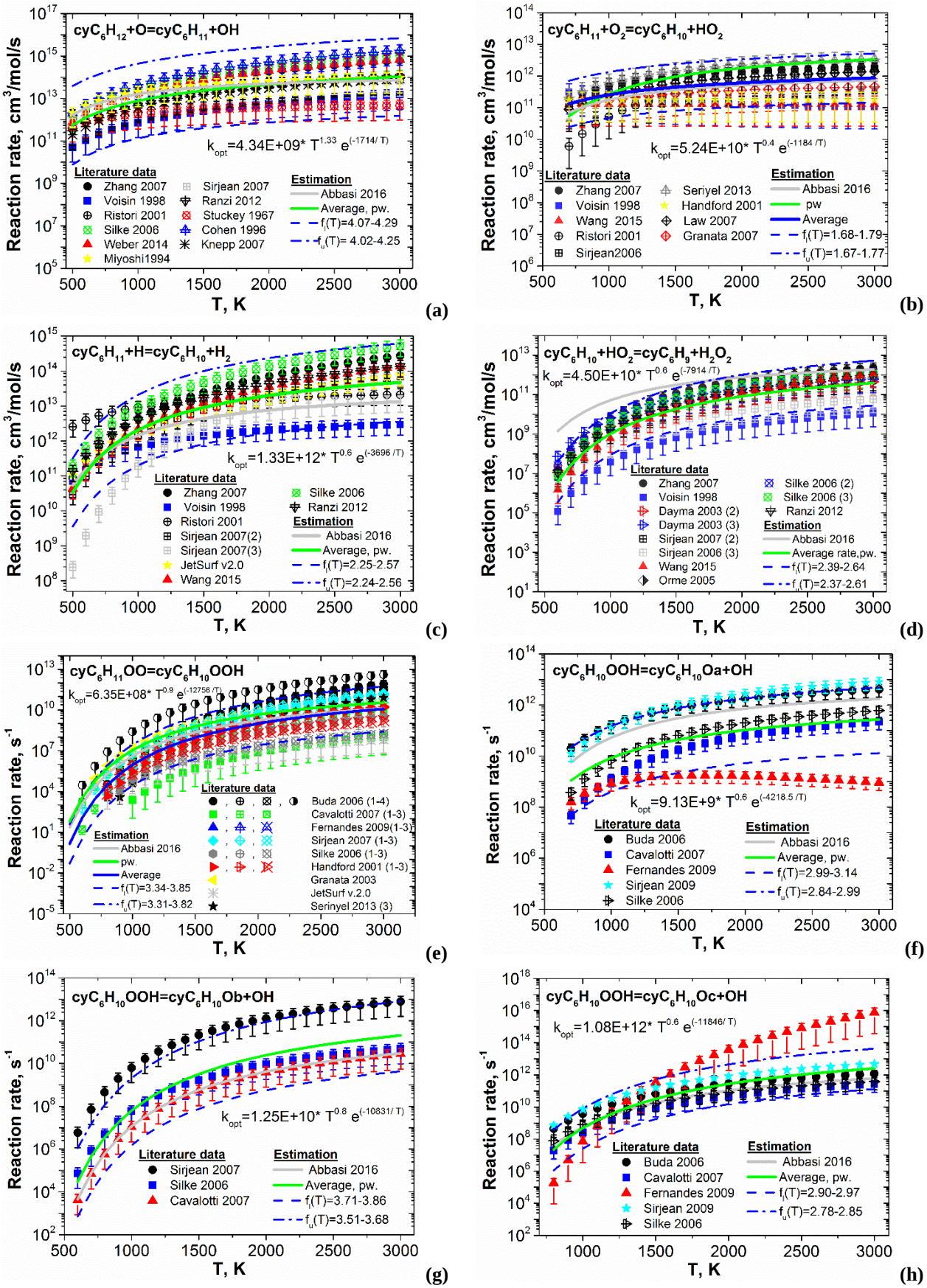


Figure 2.6 Results of the uncertainty analysis for the selected reactions based on the available literature data [9, 22-30, 34, 49-63, 72-77]. The characters written in parenthesis in front of the symbols represent the isomer types in the corresponding reference. The estimated activation energy for the average k_{opt} is in Kelvin.

In the case no uncertainty claimed for the observations, an error equal to 50% was assigned to the rate coefficient. Fig 2.6 visualizes the performed uncertainty analysis for selected reactions. In most cases, the literature data slightly disagree from each other and the uncertainty factors are in the range of 2-4. However, in certain reactions, namely $cyC_6H_{12} + O \leftrightarrows cyC_6H_{11} + OH$, $cyC_6H_{11}OO \leftrightarrows cyC_6H_{10}OOH$, and $cyC_6H_{10}OOH \leftrightarrows OH + b\text{-}cyC_6H_{10}O$ the reaction rates, reported by different sources, largely deviate from each other (Fig 2.6 a, e, g).

Table 2.2 summarizes the actual uncertainty levels of the rate coefficients of the main reaction types. As we can see, the average uncertainty factors are about 2-3. In certain cases, they even exceed this level; for instance in the case of the O_2 addition reaction (*type VII*) $cyC_6H_{11} + O_2 \leftrightarrows cyC_6H_{11}OO$ and the β-scission decomposition of the cyclohexyl hydroperoxide $cyC_6H_{10}OOH \rightarrow CH_2O + C_5H_8 + OH$ (*type X*), where the uncertainty factors have been estimated around 6.1-6.8 and 3.3-4.7, respectively.

For few reactions where no adequate observation data was available, the uncertainty analysis was not performed, for instance, the reaction $cyC_6H_{12} \leftrightarrows cyC_6H_{11} + H$. Also, for the analogous reactions, no additional uncertainty evaluation was required.

In previous work of the author [55], the rate parameters for H-atom abstraction of bi-cyclic ethers and cyclohexanone (*type XV*, Fig 2.2, *R97-R108*) were set as recommendation of Curran et al. [15] for similar reactions in iso-octane sub-mechanism. In this study, they have been recalculated, using the correlation of Eq. (2.2) and algorithm of Chernyi et al. [68]. By performing the above mentioned statistical treatment of uncertainties, the estimated average rates (k_{opt}) were further calculated and implemented in the current mechanism for these reactions. The final results of the uncertainty analysis, together with the reaction rate modifications are provided in section 5.2, Table 5.2.

Table 2.2 The lower and upper uncertainty factors of the rate coefficients of the main reaction types.

Reaction	Type	$f_l(T)$	$f_u(T)$
$cyC_6H_{12} \rightarrow 3C_2H_4$	DE, RN (I*)	2.33-3.78	0.92-2.37
$cyC_6H_{12} \leftrightarrows cyC_6H_{11} + H$	DE, INT (I)	-	-
$cyC_6H_{12} \leftrightarrows aC_6H_{12}$	RN (I)	5.88-6.20	4.85-5.17
$cyC_6H_{12}+O_2 \leftrightarrows cyC_6H_{11} + HO_2$	HABS,INT (II)	2.47-2.65	2.44-2.62
$cyC_6H_{11} \leftrightarrows C_6H_{11}$	RN (III)	2.82-2.92	2.71-2.80
$cyC_6H_{11} \leftrightarrows cyC_6H_{10} + H$	DE, DHY (VI)	3.38-3.57	3.07-3.26
$cyC_6H_{11}+O_2 \leftrightarrows cyC_6H_{10} + HO_2$	HABS, DHY (VI)	1.68-1.79	1.66-1.77
$cyC_6H_{10} \leftrightarrows cyC_6H_9 + H$	DE, DHY (VI)	3.11-3.21	2.82-2.92
$cyC_6H_{11}+O_2 \leftrightarrows cyC_6H_{11}OO$	ADD (VII)	6.40-6.83	6.1-6.58
$cyC_6H_{11}OO \leftrightarrows cyC_6H_{10}OOH$	ISM (VIII)	3.34-3.85	3.31-3.82
$cyC_6H_{10}OOH \rightarrow CH_2O + C_5H_8 + OH$	BSC, RN (X)	4.28-4.73	3.33-3.78
$cyC_6H_{10}OOH \leftrightarrows OH+cyC_6H_{10}Oa$	DE-OH (XI)	3.00-3.14	2.84-2.99
$cyOOC_6H_{10}OOH \leftrightarrows OH+ cyOC_6H_9OOH$	DE-OH (XIV)	2.87-2.92	2.77-2.82
$cyC_6H_{10}Oa+OH \leftrightarrows cyC_6H_9O+H_2O$	HABS (XV)	0.89-0.93	0.88-0.93
$cyC_6H_{11}O \rightarrow CH_2CHO + 2C_2H_4$	DE, RN (XIX)	2.65-286	2.56-2.75

Abbreviations:
DE: Decomposition **INT:** Initiation **HABS:** H atom Abstraction **RN:** Ring-opening **DHY:** Dehydrogenation **BSC:** β- Scission **ADD:** Addition **ISM:** Isomerization **DE-OH:** Decomposition to release OH
* The roman numbers in parentheses represent the reaction type, also illustrated in Fig 2.1-2.2.

3. Determination of Thermodynamic Properties

3.1. Introduction

Realistic estimations of certain thermodynamic properties, namely standard heat of formation, standard entropy and heat capacity values, as well as determination of the kinetic parameters, such as bond energy, Gibbs free energy, and reaction rates, which directly relate with the thermodynamic properties of species, are known as necessities in order to develop a combustion model for hydrocarbons. Therefore, the thermodynamic data of certain species occurring in our reaction model of cyclohexane oxidation in both high and low temperature regimes have been revised and evaluated.

3.2. Review of Existing Database and Uncertainty

A review over the thermochemistry data used in available cyclohexane kinetic models (at low and high temperatures) reveals that, the model of Silke et al. [9] includes the thermodynamic properties calculated with the THERM program of Ritter and Bozzelli [78], which implements the group additivity method of Benson [79]. Buda et al. [29] presented a kinetic model with thermochemical data calculated using the software THERGAS [80] which is also based on the group additivity method [79]. An update of this model was performed by Serinyel et al. [30], which used thermodynamic properties calculated with CBS-QB3 by Sirjean et al. [48, 49].
Sirjean et al. [49] studied the gas-phase reactions of cyclopentylperoxy and cyclohexylperoxy radicals and determined the required thermodynamic properties (14 species, see Table 1 of [49]) by quantum chemistry calculation at the CBS-QB3 level using isodesmic reactions.

Table 3.1 contains the information about the standard enthalpy of formation, and standard entropy of species involved in low temperature chemistry of current model, as well as those reported in other well-known kinetic studies of cyclohexane [9, 29, 30, 49, 48], and in the databases of the National Institute of Standards and Technology (NIST) [81] and Burcat et al. [82]. The scatter of literature data has also been evaluated and included in this table (last column). None of the sources reports data for all required species. Moreover, for certain species the uncertainty of data is remarkably high and the values differ between models and data sources, for instance in the case of the standard heat of formation of cyC_6H_{10}, $cyC_6H_{10}OOH$, and the bi-cyclic epoxies (a,b-$cyC_6H_{10}O$ particularly), which are decisive for the auto-ignition behaviour of cyC_6H_{12}. This fostered our interest to revise, evaluate thermodynamic properties with an in-house developed numerical tool to (a) complete the dataset for all species needed in the kinetic scheme and (b) to assess the uncertainty of the values obtained.

There are several methods available to calculate the thermodynamic properties of species: experimental determinations and extrapolations, quantum chemistry approaches, and (semi-) empirical methods. The latter are favoured over quantum chemistry methods in terms of computational costs. They are extensive, fast and compatible with a range of computational resources, and allow calculation of properties for large systems, especially calculating thermo-chemical data of large molecules. On the other hand, due to the dependency of empirical methods on experimental data, unlike the quantum chemistry approaches, their application is often limited.

Table 3.1 Comparison of the properties for certain low temperature intermediates used in different cyclohexane models and collected in NIST [81] and Burcat [82] databases.

Species	Silke et al. [9]		Buda et al. [29]		Serinyel et al. [30]		Sirjean et al. [49, 48]		NIST [81], Burcat [82]		*Uncertainty%*	
	ΔH_f^0*	S^0*	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0
cyC_6H_{11}	70.35	326.81	74.70	317.93	71.22	318.95	71.48	325.2	75.82[b]	317.75[b]	3.29	1.35
cyC_6H_{10}	-4.62	316.23	-	-	-5.73	310.68	-0.41	304.3	-4.32[a]	310.45[a]	61.56	1.57
$cyC_6H_{11}O$	-	-	-71.48	314.46	-71.56	314.74	-	-	-	-	0.10	0.10
$cyC_6H_{11}OO$	-87.18	378.94	-81.26	370.89	-84.21	371.25	-93.21	366.59	-	-	5.90	1.38
$cyC_6H_{10}OOH$	-31.99	402.33	-29.84	400.53	-36.22	401.92	-18.39	380.80	-	-	26.18	2.63
$cyOOC_6H_{10}OOH$	-190.32	449.34	-183.08	453.03	-185.08	453.48	-	-	-	-	2.01	0.50
$cyOC_6H_9OOH$	-339.65	409.62	-	-	-353.12	377.49	-	-	-	-	2.75	5.77
a-$cyC_6H_{10}O$	-30.52	272.51	-118.09	312.7	-126.80	322.97	-126.65	322.70	-125.52[a]	-	39.88	7.78
b-$cyC_6H_{10}O$	-37.80	261.93	-	-	-	-	-107.00	316.43	-	-	67.59	13.33
c-$cyC_6H_{10}O$	-121.6	253.44	-177.44	312.71	-183.28	313.34	-183.08	313.08	-	-	18.01	10.00
d-$cyC_6H_{10}O$	-236.80	338.24	-	-	-230.52	322.10	-232.83	334.82	-231.10 [a]	335.53[a]	1.22	2.16
cyC_6H_9-1,3	106.50	309.67	-	-	126.92	321.35	-	-	131.45[b]	313.65[b]	10.93	1.89
cyC_6H_9-1,4	109.18	291.06	-	-	192.81	322.32	-	-	-	-	39.16	7.21

* ΔH_f^0 , S^0 are in $kJ \cdot mol^{-1}$ and $J \cdot mol^{-1} \cdot K^{-1}$, *respectively*. *a*: NIST [81] *b*: Burcat [82]

Note: Also published in Abbasi et al. [83].

A combination of experimental measurements with their extrapolations was applied by Rossini et al. [84] and Wilhoit et al. [85] to estimate enthalpies and heat capacities for 38 different species. The performed calorimetric measurements were used for analytical determination of properties of the molecule structure groups. Goldsmith et al. [86] used the quantum chemistry RQCISD (T)/cc-PV∞QZ//B3LYP/6-311++G (d,p) method for 219 small molecules, including radicals, bi-radicals, and triplet species.

The group additivity method, which is based on molecular mechanics, was developed by Benson et al. [79, 87, 88, 89] and contains mainly hydrocarbons and a few contributions for oxygenated groups. This was further extended to free radicals by O'Neal et al. [90]. The Benson group additivity is easy to apply and it allows estimation of properties with an acceptable uncertainty compared to experimental data. This method has been also applied in present work. However, there are several groups in hydrocarbon molecules either with only partially determined or completely unknown properties. Sabbe et al. [91, 92] have estimated Benson group values for the standard formation enthalpy (at T = 298 K and p = 1 atm), entropy and heat capacity of 95 Benson groups, related to alkenes, alkynes, aromatics, radicals and hydrogen bond increments (HBI). The standard heat of formation ΔH_f^0 has been calculated, using ab-initio values at CBS-QB3 level [91]. For the estimation of standard entropy S^0 and heat capacity $C_p(T)$ a set of B3LYP/-6-311G (d, p) ideal gas statistical properties were used [92]. Also, the ring strain corrections for 7 cycloalkanes and 12 cycloalkenes were estimated based on ab-initio methods [92]. The computational results have been compared with experimental values for 39 species. The estimated groups demonstrated an acceptable consistency with the available literature data; see e.g. Benson et al. [79, 87-89] and Cohen et al. [93].

An update of thermochemical Benson groups has been delivered by Khan et al. [94], who estimated thermodynamic properties for 323 different species including oxygenated compounds and radicals. They performed quantum chemical calculations, conducted with B3LYP functional and using Gaussian-3 theory. From these estimations, 122 new different Benson additivity groups and 21 gauche and cis corrections were extracted. In the work of Bhattacharya et al. [95] values of the standard formation enthalpy for a set of oxygen-containing radicals and alkyl groups were evaluated. Their estimation methods are empirical and semi-empirical, based on information from well-established smaller species or from analogy with similar groups. However, some other types of unknown groups, i.e. radicals of oxygenated compounds and radicals of multiple bound structures, remained unknown.

In this work, based on the group additivity method of Benson et al. [79], the standard heat of formation ΔH_f^0, the standard entropy S^0, and the heat capacity $C_p(T)$ have been evaluated for oxygenated cyclohexane species and for certain Benson additivity groups found in the structure of studied molecules and transient complexes. The properties for certain number of these groups and species, were not found in our comprehensive literature review [79, 87-96], and are only available in the quantum chemistry calculations [91, 92, 94].

Therefore, the current chapter is organized as follows: The first part describes the utilized approaches for estimation of the properties of new Benson groups. The second part highlights the estimation of ring correction groups. In the next section, comparisons of new estimated properties of ten Benson groups with quantum chemistry calculations reported by Khan et al. [94] are provided. The following section (see section 3.4) presents results of comparisons of the predicted thermochemistry data (present work, p.w.) and previously published literature values

for a select list of species. It contains only the species, which contain at least one of the newly calculated groups. The validation of the introduced ring corrections for certain ring structures are then described and compared with available literature data. The next section describes the final step of the applied methodology validation: thermochemical properties for some species of the cyclohexane low temperature chemistry used in other kinetic models or presented in databases were estimated and compared with literature values. In the last part of this chapter, the conclusions and tables of calculated properties are presented.

3.3. Estimation of Properties with the Benson Additivity Method

3.3.1. Determination of Properties of the New Groups

To evaluate the values for the standard enthalpy of formation ΔH_f^0, standard entropy ΔS^0, and heat capacity $C_p(T)$ terms for new Benson groups (G1-G17) in Table 3.2 and the [C-(C_d)(CO)(H_2)] group, an empirical approach was used. This combinative approach is based on the Benson contribution rules and direct estimations of thermodynamic properties [97].

To explain this approach, the estimation of properties of the new unknown group [C·-(O)(H_2)] will be described in detail. It is a radical-centered group, representing a radical of carbon, bonded with oxygen and two other hydrogen atoms. Firstly, the appropriate "parent" (or reference) molecule has to be found. In this case, it would be the CH_2COCH_3 molecule, which consists of this unknown group, and two other known Benson groups: [O-(C)(C·)] and [C-(O)(H_3)]. Based on the additivity rules, the ΔH_f^0 of the unknown group can be estimated as the difference between the enthalpy of the parent molecule and the known groups:

$$\Delta H_f^0[\text{C·-(O)(H}_2\text{)}] = \Delta H_f^0[\text{CH}_3\text{OCH}_2] - \Delta H_f^0[\text{O-(C)(C·)}] - \Delta H_f^0[\text{C-(O)(H}_3\text{)}] \qquad Eq\ (3.1)$$

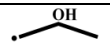
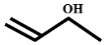
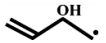
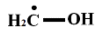
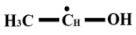
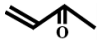
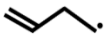
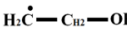
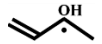
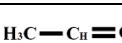
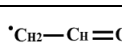
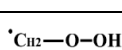
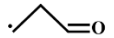
The S^0 and $C_p(T)$ values are estimated in a similar way. Table 3.2 provides a list of 17 newly introduced groups and their thermodynamic properties within the range 300-1500 K, along with their parent compounds. The parent (reference) molecules have been selected to be the simplest available and not larger than C_5, with the aim to reduce the uncertainty of calculations.

However, the mentioned method is not appropriate for the [C-(C_d)(CO)(H_2)] group, which is one of the constructive groups of the transient complexes cyC_6H_8O with one conjugated carbon bond and a carbonyl group, since no "parent" molecules with completely "known" properties can be found. The best matching case for a reference molecule could be 3-butenal. Its properties are partially known and have the potential to be completed and improved using different strategies, which are described in the following section.

3.3.2. Determination of Properties of the [C-(C_d)(CO)(H_2)] Benson Group

Three different methods are considered to derive ΔH_f^0, S^0 and $C_p(T)$ of the [C-(C_d)(CO)(H_2)] group from the properties of the "parent" molecule: *i) Additivity of Bond Properties, ii) Statistical Mechanical Estimation,* and *iii) Group Contribution Method*.

Table 3.2 The newly determined groups via the combination method [83].

No.	Group	ΔH_f^0 / kJ·mol^{-1}	S^0 / J·mol^{-1}·K^{-1}	$C_p(T)$ /J·mol^{-1}·K^{-1}							Reference Species	Structure	Ref.
				300	400	500	600	800	1000	1500			
G1	C-(C•)(C)(O)(H)	-10.77	-49.75	24.63	30.87	35.06	38.28	41.67	42.00	47.20	C_3H_7O		[98]
G2	C-(C_d)(C)(O)(H)	-43.42	-55.59	16.35	26.37	34.24	40.10	45.71	44.82	47.26	C_4H_8O-(s)		[98]
G3	C-(C_d)(C•)(O)(H)	-12.40	-43.94	14.01	23.14	30.79	36.87	43.14	43.14	46.48	$CH_2CH[OH]C_2H_3$		[98]
G4	C•-(O)$(H)_2$	147.50	127.10	26.19	29.00	32.90	36.16	39.90	44.04	50.15	CH_3OCH_2		[82]
G5	O-(C•)(H)	-148.06	126.00	22.28	25.00	26.23	27.57	31.39	33.35	37.30	CH_2OH		[82]
G6	C•-(C)(O)(H)	134.68	41.09	15.76	19.00	23.41	27.09	30.58	32.07	34.66	CH_3CHOH		[98]
G7	CO-(C_d)(C)	-146.52	52.20	24.72	29.61	34.06	37.86	41.10	42.36	45.75	C_4H_6O (717)		[98]
G8	C•-(CO)$(H)_2$	140.44	126.21	23.82	28.54	32.59	36.08	40.40	44.06	49.00	CH_2COCH_3		[82]
G9	C-(C•)(C_d)$(H)_2$	-25.19	37.95	21.18	26.64	32.71	38.19	45.61	51.44	59.95	C_4H_7 (3-buten-1-yl)		[82]
G10	C•-(C_d)$_2$(H)	81.19	25.46	16.60	24.20	30.87	35.66	40.85	45.86	50.07	C_5H_7 (1,4-pentadien-3-yl)		[82]
G11	C-(C•)(O)$(H)_2$	-32.41	42.88	18.29	25.82	31.50	36.42	44.20	52.29	61.38	CH_2CH2OH		[82]
G12	C•-(C)(C_d)(O)	84.01	-59.86	11.28	15.31	19.96	23.24	24.86	25.52	27.17	$CH_3C[OH]CHCH_2$		[98]
G13	CO=C	-84.75	126.70	30.39	3 2.81	34.38	35.28	36.73	37.71	39.06	CH_2CO		[82]
G14	CO-(C)(H)	-123.81	137.04	29.60	33.23	37.20	41.00	46.63	50.80	56.00	CH_3CHO		[82]
G15	CO-(C•)(H)	-115.24	141.92	31.31	34.83	38.37	41.72	48.73	53.61	62.35	CH_2CHO		[98]
G16	O-(C•)(O)	-11.51	32.92	15.40	19.63	22.25	24.71	29.69	30.80	34.62	CH_2OOH		[98]
G17	C-(CO)(C•)$(H)_2$	-7.43	51.38	23.17	28.71	33.11	37.05	44.06	50.21	56.62	C_3H_5O-J(13)		[98]

*Deviations for ΔH_f^0 are assumed to be $\pm$5 kJ·mol^{-1}, whereas uncertainties for S^0 and $C_p(T)$ are assigned to be about $\pm$10 J·mol^{-1}·K^{-1}, due to implemented combinative approach and the recommendation of Benson [79] for additivity method, and considering 10% of uncertainty for parent molecule from literature.

None of these methods can provide a full set of required thermodynamic data. Only using them in combination enables us with final estimation of this group. The results, obtained with methods i)-iii), have been compared with each other and with the average values. The predicted uncertainties have been assigned to each new group, see Table 3.4.

i) Additivity of Bond Properties

Based on this method, developed by Benson 1976 [79], in the standard condition (p=1 atm, T=300 K) the properties of gas phase species can be estimated from their bond contribution properties. A list of bond contributions has been provided in Table 2.1, p.25 of [79]. This method is applicable to approximate ΔH_f^0 with an accuracy of 10 kJ·mol^{-1}, and for S^0 and C_p^0 with accuracy of 5 J·mol^{-1}·K^{-1}. A larger error in the case of heavy branched structures is expected. Moreover, bond additivity is not able to distinguish the property differences between isomers. With this method, ΔH_f^0, S^0 and C_p^0 of 3-butenal have been calculated only at the standard condition in units kJ·mol^{-1} and J·mol^{-1}·K^{-1}, respectively (see *Appendix IV, Sheet 1).*

ii) Statistical Mechanics Estimation

This method can estimate the standard entropy and heat capacities with reliable uncertainties [79], but it is not able to approximate the standard heat of formation directly. According to statistical mechanics, thermodynamic data of compounds can be described via several partition functions, obtained from contributions of four degrees of freedom: translational, rotational, vibrational and electronical [79]. Except in the case of low-lying electron states or non-zero spin, and radicals or molecules with odd numbers of electrons, the effects of the electronic partition can be neglected. With certain assumptions, such as those of an ideal gas, non- linearity of the molecule and neglecting quantum effects, the heat capacity would be mainly described by its vibrational contribution [79]:

$$C_p \cong 4R + C_{p,vib} \quad , \quad C_{p,vib} = R \cdot x^2 e^x/(e^x - 1)^2 \qquad Eq\ (3.2)$$

where $x = hcv/k_bT$ is a dimensionless scalar, representing vibrational frequencies, h is Planck's constant, c is the speed of light and k_b is the Boltzmann constant. The values for x at different temperatures were tabulated and are available in Benson, 1976 [79]. Similarly, the standard entropy can be determined with its translational, rotational and vibrational contributions. For simplification of estimations, the properties of the target molecule ϕ_{target} can be calculated through two terms: properties of the model (or reference) molecule ϕ_{model}, with an analogous structure and known properties, and a correction $\Delta\phi$ calculated as the partition functions for differences in translational, rotational and vibrational contributions:

$$\phi_{target} = \phi_{model} + \Delta\phi \qquad Eq\ (3.3)$$

The model molecule is preferably the closest molecule in structure and mass to the parent molecule (3-butenal). In this case it is 1,4-pentadiene (1,4-C_5H_8), for which all required properties are available (Fig 3.1).

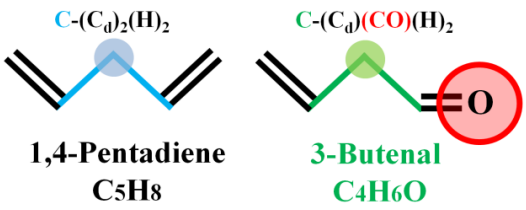


Figure 3.1 Comparison between structures of the unknown group [C-(C_d)(CO)(H_2)] (green) and [C-(C_d)$_2$(H_2)] (blue) [83].

Therefore, for each entropy contribution, and for heat capacity vibrational contribution ($\Delta C_{p,vib}$) the correction terms are calculated. The total correction of standard entropy will be the summation of the corrections for each translational (ΔS^0_{tran}), rotational (ΔS^0_{rot}) and vibrational (ΔS^0_{vib}) contribution. Since the translational contribution varies as $\frac{3}{2} R \ln M$ where M (g·mol^{-1}) is the molecular weight, ΔS^0_{tran} can be estimated as follows [79]:

$$\Delta S^0_{tran} = \frac{3}{2} R \ln \left(\frac{M_{target}}{M_{model}}\right) \qquad Eq\ (3.4)$$

The rotational contributions vary as $\frac{1}{2} R \ln (I_x I_y I_z)$ where I_x , I_y and I_z are the three principal moments of inertia of the molecule. Since in our case, there is not any significant difference between the model and target molecules in distance of the mass of heavier atoms, and also in the axial distances from centre of gravity, ΔS^0_{rot} would be considered negligible [79].

The vibrational contribution of entropy and heat capacity are highly dependent on stretching and bending frequencies. Therefore, both terms of ΔS^0_{vib} and $\Delta C_{p,vib}$ follow the differences in vibrational frequencies of the model and target molecules, i.e. 1,4-C_5H_8 and 3-C_4H_6O, respectively. The model molecule (1,4-C_5H_8) has six additional stretching and deformation frequencies compared to 3-butenal, which makes the ΔS^0_{vib} the largest contribution of the overall ΔS^0 between target and model molecule. Also the symmetry difference between 1,4-C_5H_8 and 3-C_4H_6O and its influence on entropy should be taken into account.

The correction due to this feature, known as symmetry correction is obtained by subtracting $R \ln \sigma$, where σ is the symmetry number [79]. Thus, the symmetry difference between the model and target molecule is evaluated as follows:

$$\Delta S_{sym} = R \ln \frac{\sigma_{model}}{\sigma_{target}} \qquad Eq\ (3.5)$$

The details of calculations for both heat capacity values and standard entropy in unit J·mol^{-1}·K^{-1}, are provided in *Appendix IV* (see *Sheet 2*); the final results of statistical mechanics estimations for 3-C_4H_6O are summarized in Table 3.3 in standard units.

iii) Group Contribution Method

This method was developed by Joback et al. [99] and can estimate eleven physical properties, including standard enthalpy of formation and heat capacities over temperature ranges by a family of group-contributions. Lists of the architectural groups with their properties and the estimation equations are available in Tables 2-3 in pp. 234-238 of [99]. 3-C_4H_6O contains the following groups: (=CH_2), (=CH-), (-CH_2-), (O=CH-). The values for ΔH_f^0 and $C_p(T)$ are estimated with this method and equations described in [99].

The details of the calculations with the mentioned methods are provided in *Appendix IV*, *Sheet3.* The final results of the Group Contribution Method application to 3-C_4H_6O are summarized in Table 3.3.

Table 3.3 Thermodynamic properties of 3-C_4H_6O calculated with three semi-empirical methods [83].

Method	ΔH_f^0 / kJ·mol^{-1}	S^0 / J·mol^{-1}·K^{-1}	$C_p(T)$ /J·mol^{-1}·K^{-1}						
			300	**400**	**500**	**600**	**800**	**1000**	**1500**
i) Benson Bond energy	-83.64	330.95	91.13	-	-	-	-	-	-
ii) Statistical Mechanics	-	341.32	94.22	116.6	134.6	149.4	172.1	188.8	213.6
iii) Joback & Reid	-85.98	-	91.63	112.7	130.8	146.2	170.5	187.9	217.6

After estimation of the properties of the parent molecule 3-C_4H_6O (Table 3.3), the properties of target group [C-(C_d)(CO)($H)_2$] can be calculated though application of the combination rule. Table 3.4 presents the results for the properties of this group, by applying *Additivity of Bond Properties, Statistical Mechanics and Estimation and Group Contribution* methods. The mean values of results of these three methods are set as the reported properties (marked with bold numbers), and the standard deviations are considered as uncertainty of calculation (written in *italic*). Details of approximations are included in the *Appendix IV*, see *Sheet 4* and *Sheet 5.*

Table 3.4 Properties for [C-(C_d)(CO)($H)_2$] by different methods [83].

Method used for properties of parent molecule 3-C_4H_6O	ΔH_f^0/ kJ·mol^{-1}	S^0 / J·mol^{-1}·K^{-1}	$C_p(T)$ /J·mol^{-1}·K^{-1}						
			300	**400**	**500**	**600**	**800**	**1000**	**1500**
i)Benson Bond energy	-24.02	36.07	23.10	-	-	-	-	-	-
ii)Statistical Mechanics	-	46.43	26.20	36.26	42.11	46.04	51.09	55.25	62.04
iii)Joback & Reid	-26.38	-	23.60	32.39	38.24	42.90	49.48	54.32	66.17
Final values*	**-25.20** *±1.20*	**41.25** *±7.30*	**24.30** *±1.40*	**34.33** *±1.90*	**40.17** *±1.90*	**44.47** *±1.6*	**50.28** *±0.8*	**54.78** *±0.5*	**64.10** *±2.1*

* Uncertainty values are assigned to be equal to estimated standard deviation of all methods.

Since most of the studied intermediates related to the low and high temperature oxidation sub-mechanism of cyclohexane species are cyclic, the 18 newly determined groups are insufficient to estimate their properties, and the influence of a ring structure on the thermodynamic properties has to be estimated.

3.3.3. Ring Strain Correction Groups

The strain energy term is often used in the case of highly branched or cyclic molecules [79]. Most of the ring structures require unique strain corrections, which cannot be derived from groups themselves [92]. However, this term can be considered as an additive value to the strain energy of unbranched hydrocarbons, defined as "unstrained" and assigned to be zero [79]. On these grounds, the difference between the (experimentally) observed ΔH_f^0 and the formation enthalpy estimated from the unstrained standard group additivity is assigned as the strain energy [79]. Cohen et al. [100] used the same approach:

$$\Delta H_f^0\ (C_nH_{2n}) = n\cdot[\ \Delta H_{f,s}^0] + F_n \qquad Eq\ (3.6)$$

where $\Delta H_{f,s}^0$ represents enthalpy of formation of each [C-$(C)_2(H)_2$] group, n is the number of [C-$(C)_2(H)_2$] groups, and F_n is equal to strain energy value. For the species with different groups in rings, the strain energy can also be defined as the difference between the standard formation enthalpy following from measurements or literature data and that from summation of the constructing groups. A similar approach can also be applied for S^0 and $C_p(T)$ to evaluate the correction groups. Therefore, with the properties of the known species, reported in the literature, the correction factor can be calculated. For few cyclic species, such as cyclohexane and oxirane, they have been already estimated by Benson et al. [87]. Sabbe et al. [91] evaluated ring strain corrections for 18 species differing from each other by size of the rings (number of the carbon atoms in the ring), and numbers and the locations of the endocyclic double bonds (see Table 6 of [91]). A study by Lay et al. [101] has estimated thermodynamic properties for 34 oxygenated hydrocarbons, using PM3 calculations, and extracted the ring correction groups with the aid of additivity groups. However, most of these estimations are only available for the ring strain energy (ΔH_f^0 correction), or only available for cyclic oxygenated compounds, such as oxirane or hydropyrane. Therefore, the required correction groups have to be estimated or re-estimated based on recent available sources, which is a part of the current work. Table 3.5 contains the calculated correction factors F_n for properties of different cyclic molecules, RC1-RC9.

The group RC10 presents the ring correction for each member sitting in the cyclohexane ring. This correction is used to estimate the properties of multi-cyclic molecules. For example, the bicyclic a-cy$C_6H_{10}O$ molecule is in fact a cyclic ether with three members, forming an external hydrocarbon ring with 4 other carbons. For this structure, the correction factor is considered to be an oxirane correction (RC1), added with 4 cyclohexane corrections RC10 (for each carbon atom).

Table 3.5 Estimated ring correction groups * [83].

No.	Species	Ref.	Structure	ΔH_f^0/ kJ·mol^{-1}	S^0/ J·mol^{-1}·K^{-1}	$C_p(T)$ /J·mol^{-1}·K^{-1}						
						300	**400**	**500**	**600**	**800**	**1000**	**1500**
RC1	Oxirane	[102]		114.27	135.8	-8.66	-11.0	-10.0	-8.66	-8.45	-7.28	3.47
RC2	Oxetane	[82]		106.0	123.1	-16.8	-19.3	-16.6	-13.0	-11.1	-8.33	4.73
RC3	Hydro furan (iv)	[82]		23.05	111.1	-25.3	-25.6	-20.9	-15.8	-11.9	-7.91	6.11
RC4	Hydro Pyran (iv)	[82]		3.10	70.96	-28.0	-28.3	-23.4	-17.8	-12.4	-7.28	7.70
RC5	Oxepane	[103]		27.11	77.36	-25.6	-22.4	-16.0	-10.6	-3.9	1.13	18.20
RC6	Cyclohexane	[81]		-3.86	75.71	-31.94	-25.91	-18.27	-11.47	-0.83	4.60	9.45
RC7	Cyclohexene	[81]		3.73	87.87	-21.51	-18.01	-13.89	-10.72	-5.86	-3.13	2.11
RC8	1,3-cyC$_6$H$_8$	[82]		17.70	107.0	-20.2	-20.5	-17.1	-13.1	-8.95	-5.56	-2.47
RC9	1,4-cyC$_6$H$_8$	[82]		1.54	29.1	-14.32	-14.28	-11.08	-7.66	-4.86	-2.81	-0.59
RC10	CHX/6**	[81]		-0.64	12.62	-5.32	-4.32	-3.05	-1.91	-0.14	0.77	1.58

*Deviations for ΔH_f^0 are $\pm$13.0 kJ·mol^{-1} and uncertainties for S^0, $C_p(T)$ are assigned to be about $\pm$7.0 J·mol^{-1}·K^{-1}, for heavy substituted species. **Correction factor for each C atom in the cyC$_6$H$_{12}$ ring is based on the values reported in [87].

3.4. Results and Discussion

3.4.1. Validation and Results

For ten newly estimated groups (see Table 3.6), namely: G1, G4, G6, G7, G8, G10, G12, G15, G14 and G16, literature data is available: Sabbe et al. [91, 92] estimated the group properties using ab-initio quantum chemistry methods; the data of Khan et al. [94] has been evaluated based on the estimated properties of the reference species, using Gaussian-3 theory with B3LYP geometries; Da Silva and Bozzelli [104] determined certain group additivity values for the carbon-oxygen-hydrogen groups important to aldehydes. They achieved this by estimating properties of certain reference aldehyde molecules, using the G3, G3B3, and CBS-APNO theoretical methods. Table 3.6 provides a comparison of our calculated properties with those estimated in [91, 92, 94, 104]. The differences between predicted values and those reported in literature are on average 6.2 kJ·mol^{-1} for ΔH_f^0, 8.5 J·mol^{-1}·K^{-1} for S^0, and 6.75 J·mol^{-1}·K^{-1} for C_p over the temperature range of 300-1500 K. The maximum deviation is seen in the case of G1, where the deviations in ΔH_f^0, S^0 and $C_p(300\ K)$ are 19.28 kJ·mol^{-1}, 15.40 J·mol^{-1}·K^{-1}and 16.22 J·mol^{-1}·K^{-1}, respectively. Also the data for G12 and G16, despite of their good agreement with Khan et al. [94] in ΔH_f^0 values, deviate significantly in C_p. The main reasons for these deviations could be due to the existing uncertainty in the thermochemistry of the reference species.

Table 3.6 Comparison of thermodynamic additivity groups between present work (p.w.) and literature data [83].

No.	Group	Ref	ΔH_f^0 / kJ·mol^{-1}	S^0 / J·mol^{-1}·K^{-1}	$C_p(T)$ /J·mol^{-1}·K^{-1}						
					300	**400**	**500**	**600**	**800**	**1000**	**1500**
G1	C-(C•)(C)(O)(H)	p.w.*	-10.77	-49.75	24.63	30.87	35.06	38.28	41.67	42.00	47.20
		[94]	-30.05	-59.65	32.98	39.38	42.89	45.06	47.69	49.12	51.16
G4	C•-(O)(H)$_2$	p.w.	142.50	127.10	26.19	29.00	32.90	36.16	39.90	44.04	50.15
		[94]	139.78	130.17	25.37	30.68	36.16	40.38	45.06	49.20	55.89
G6	C•-(C)(O)(H)	p.w.	134.68	41.09	15.76	19.00	23.41	27.10	30.58	32.07	34.66
		[94]	140.66	46.90	20.61	25.87	30.01	33.06	36.45	38.87	42.22
G7	CO-(C$_d$)(C)	p.w.	-146.52	52.20	24.72	29.61	34.06	37.86	41.10	42.36	45.75
		[94]	-136.73	65.75	25.00	25.58	27.09	28.67	32.19	36.12	45.02
G8	C•-(CO)(H)$_2$	p.w.	140.44	126.21	23.82	28.55	32.60	36.08	40.40	44.06	47.91
		[94]	143.67	121.30	27.96	34.40	38.83	42.18	47.19	51.41	55.68
G10	C•-(C$_d$)$_2$(H)	p.w.	81.19	25.46	16.60	24.20	30.87	35.66	40.85	45.86	50.07
		[91, 92]	76.57	16.48	17.36	25.77	31.59	35.48	40.29	43.35	47.66
G12	C•-(C)(C$_d$)(O)	p.w.	84.01	-68.99	11.28	15.32	19.97	23.24	24.86	25.52	26.06
		[94]	83.77	-53.59	27.50	33.23	35.28	35.91	35.45	34.94	35.45
G14	CO-(C)(H)	p.w.	-123.81	137.04	29.60	33.23	37.20	41.00	46.63	50.80	56.00
		[104]	-123.18	145.88	29.26	32.60	36.78	40.55	46.82	51.00	58.10
G15	CO-(C•)(H)	p.w.	-115.24	141.92	31.31	34.83	38.37	41.72	48.73	53.61	62.35
		[94]	-128.83	146.72	28.13	31.48	35.57	39.46	45.94	50.29	59.82
G16	O-(C•)(O)	p.w.	-11.51	32.92	15.40	19.63	22.25	24.71	29.69	30.80	34.62
		[94]	-13.08	42.13	24.75	24.29	22.78	21.86	22.57	22.91	23.74

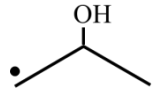
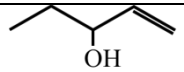
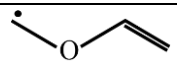
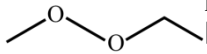
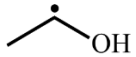
Further validations of the estimated properties of groups have been provided by comparison of the calculated thermochemistry of selected species with literature data. They have been summarized in Table 3.7. The selected species contain at least one of the new calculated groups of Table 3.2. In most cases, the values estimated in this work (p.w.) and the literature values mainly evaluated by quantum chemistry methods were consistent. The mean absolute deviations (MAD) between the present work values and the observations were also calculated for each validation case. In the case if only one set of observation was available, then the difference (DF) between calculation and literature data was provided. For all species, except C_3H_7O and C_4H_7O, the MAD or DF of standard heat of formation is less than 10 kJ·mol^{-1}, and for $S^0$and $C_p(T,K)$ is mostly less than 5 J·mol^{-1}·K^{-1}, which are satisfactory deviations. Of note, in the case of propan-2-ol-1-yl (C_3H_7O), which contains the new estimated group *G1*, the properties estimation revealed a good agreement with data from Khan et al. [94]. Except the data from Holmes et al. [105], who measured the ΔH_f^0 of C_3H_7O around -96.14 kJ·mol^{-1}, other observations were well aligned with the estimated properties, including $S^0$and $C_p(T)$ of this molecule.

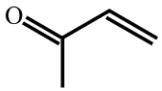
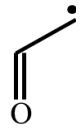
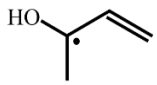
The $C_3H_7O_2$ molecule contains two new groups: G4 and G16. The estimated values for G16 disagree with the reported values from Khan et al. [94] by around 30%. Despite that, the prediction provided by this work agrees well with the mentioned reference, except at 1500 K where the heat capacity is over-predicted by around 11 J·mol^{-1}·K^{-1}. The discrepancy arises due to the estimation of 1-buten-3-ol-yl. The C_4H_7O radical contains the G12 group, where the largest disagreement between calculated properties and literature data was shown (Table 3.6). The standard heat of formation and heat capacities estimated in the current study and those provided by Hansen et al. [98] are in good agreement. But they deviate from the prediction of Khan et al. [94] by 15.65 kJ·mol^{-1} for ΔH_f^0 and by 10 J·mol^{-1}·K^{-1} for $C_p(T)$ at lower temperature.

A comparison of the predictions with the data available in literature is provided in Table 3.8. The selected species are well-studied cyclic molecules, which contain the estimated ring correction groups of Table 3.5. Similar to Table 3.7, the MAD and DF values were calculated. It has been shown that, as species become more complex in structure, the uncertainty among literature data grows as well. For example in the case of oxetane, 3-methylene (C_5H_6O), two different data sets in the Reaction Mechanism Generator (RMG) database [106] are available. They disagree on the values of the standard heat of formation by around 20.00 kJ·mol^{-1}, although they are well-matched in prediction of S^0 and $C_p$values. Also, the estimations of ΔH_f^0 , provided by Sabbe et al. [91], are higher than other references in most cases. Nevertheless, it can be seen from this table that, in the case of ring-structured species, the provided estimations in the current study stay within an acceptable margin in comparison to other available data, and are capable of predicting the thermodynamic properties of the studied ring classes.

Fig 3.2 shows the heat capacities for cyC_6H_{11}, cyC_6H_{10}, $cyC_6H_{11}O$, $cyC_6H_{11}OO$, $cyC_6H_{10}OOH$, $cyOOC_6H_{10}OOH$ and a,d-cyC_6H_{10} reported in other cyclohexane kinetic models, literature data, and calculated in this work with the newly estimated groups and ring correction factors.

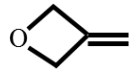
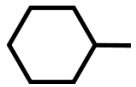
Table 3.7 Comparison of calculated and literature data for thermodynamic values of selected species containing certain additivity groups [83].

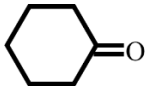
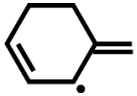
New Group	Formula	Molecule	Ref	ΔH_f^0/ kJ·mol^{-1}	S^0 / J·mol^{-1}·K^{-1}	$C_p(T)$ /J·mol^{-1}·K^{-1}						
						300	**400**	**500**	**600**	**800**	**1000**	**1500**
G1	C_3H_7O		p.w.*, [98]**	-61.71	320.43	93.30	112.57	129.23	143.49	165.00	179.34	205.61
			[94]	-64.92	319.52	96.89	115.41	131.13	144.29	165.07	180.99	206.78
			[106] [a]	-61.56	326.06	94.21	112.85	128.48	141.87	163.18	179.66	204.97
			[106][b]	-64.79	318.39	95.64	113.99	129.75	142.87	163.56	179.41	205.36
			[105]	-96.14	-	-	-	-	-	-	-	-
			[86]	-61.446	325.62	94.89	112.86	128.33	141.70	162.60	178.90	205.24
MAD [c]				***12.48***	***3.20***	***1.22***	***1.06***	***1.01***	***0.98***	***0.99***	***0.71***	***0.63***
G2	$C_5H_{10}O$		p.w.	-184.19	372.37	121.62	154.53	183.75	208.87	250.98	268.23	304.96
			[106] [d]	-191.46	385.24	125.46	157.15	183.76	206.56	242.79	269.24	301.77
DF [e]				***7.27***	***12.87***	***3.84***	***2.62***	***0.01***	***2.31***	***8.19***	***1.01***	***3.19***
G4	C_3H_5O		p.w.	90.21	303.07	79.07	92.10	103.94	114.62	135.19	145.65	166.68
			[106]	96.36	305.36	79.28	97.02	110.75	122.07	140.26	153.09	171.13
DF[e]				***6.15***	***2.29***	***0.21***	***4.91***	***6.81***	***7.45***	***5.06***	***7.44***	***4.45***
G4, G16	$C_3H_7O_2$		p.w.	36.10	358.33	103.37	125.64	144.53	161.08	188.09	205.90	241.85
			[94]	31.39	359.94	110.60	130.46	148.01	162.81	186.05	203.32	229.98
			[106]	28.38	341.46	107.47	130.71	150.15	166.32	192.36	213.10	239.68
MAD				***3.18***	***8.36***	***2.96***	***2.33***	***2.31***	***2.18***	***2.63***	***4.14***	***5.16***
G6	C_2H_4OH		p.w., [98]**	-55.53	285.13	63.67	76.80	88.93	99.80	116.42	125.12	144.89
			[106]	-55.52	284.79	64.87	77.70	89.26	99.51	115.71	126.93	145.93
			[106] [f]	-54.04	288.94	64.02	76.59	88.14	98.26	113.65	125.60	144.44
			[94]	-58.65	285.08	65.33	78.25	90.12	100.28	116.20	128.16	147.09
			[105]	-60.61	-	-	-	-	-	-	-	-
			[86]	-54.34	284.66	66.04	78.58	89.87	99.48	115.37	127.07	145.88
			[107]	-53.17	-	-	-	-	-	-	-	-
			[45]	-63.95	-	-	-	-	-	-	-	-
			[108]	-55.18	-	-	-	-	-	-	-	-
			[109]	-51.41	280.48	-	-	-	-	-	-	-
			[110]	-53.92	288.44	-	-	-	-	-	-	-
MAD				***3.47***	***2.66***	***0.86***	***0.78***	***0.70***	***0.67***	***0.98***	***1.09***	***0.92***

G7	C_4H_6O		p.w., [98]**	-127.02	321.00	87.56	109.43	129.19	146.05	170.16	187.94	212.38
			[94]	-109.93	322.82	90.37	111.27	130.04	145.88	170.38	187.97	214.35
			[106] *f*	-109.47	327.80	87.49	106.17	124.19	139.86	165.19	184.21	209.29
			[81]	-115.00	320.34	-	-	-	-	-	-	-
MAD				***7.07***	***2.92***	***1.34***	***2.11***	***2.58***	***2.88***	***2.39***	***1.77***	***2.08***
G8,G15	CH_2CHO		p.w., [98]**	25.20	268.13	54.96	63.37	70.96	77.80	89.13	97.68	111.28
			[94]	14.00	260.75	54.97	65.12	74.07	81.55	93.26	101.91	114.99
			[106] *a*	18.52	258.53	53.17	63.87	73.11	80.76	92.92	101.11	114.32
			[106] *f*	12.74	264.16	54.32	64.83	73.88	81.38	91.94	99.71	111.26
			[86]	18.39	258.74	53.09	63.95	73.15	80.67	92.38	101.16	114.53
			[109]	10.45	267.52	-	-	-	-	-	-	-
			[104]	15.50	-	-	-	-	-	-	-	-
			[111]	40.45	-	-	-	-	-	-	-	-
MAD				***4.83***	***4.23***	***0.92***	***0.64***	***1.14***	***1.42***	***1.64***	***1.64***	***1.46***
G9	C_4H_7		p.w., [82]**	204.74	317.28	84.76	104.57	122.90	138.97	167.01	181.87	209.29
			[91, 92]	217.20	324.10	84.40	104.40	122.30	137.50	161.50	179.60	210.80
			[106] *b*	208.12	315.46	86.69	105.92	123.31	138.15	161.81	179.70	208.12
			[106] *f*	204.36	321.94	82.76	103.37	121.76	137.44	162.56	180.70	209.38
			[106] *g*	203.20	320.17	88.21	109.31	126.96	141.91	165.22	182.66	210.25
			[86]	208.16	315.59	86.53	105.75	123.31	138.36	161.77	179.74	208.16
			[109]	214.43	316.01	-	-	-	-	-	-	-
			[110]	204.40	316.84	-	-	-	-	-	-	-
MAD				***4.82***	***3.04***	***1.78***	***1.89***	***1.67***	***1.52***	***2.07***	***1.18***	***0.99***
G10	C_5H_7		p.w., [82]**	205.43	323.13	93.88	119.48	141.87	160.83	188.63	209.45	239.67
			[91, 92]	209.00	308.10	95.40	121.10	143.10	161.10	188.00	208.00	240.42
			[106] *g*	205.47	323.01	94.05	120.61	142.63	161.20	189.94	215.21	239.00
			[106] *f*	206.27	317.69	86.74	115.41	138.56	157.58	186.19	207.08	237.67
MAD				***1.46***	***6.25***	***3.39***	***2.24***	***1.78***	***1.51***	***1.35***	***3.15***	***1.13***
G12	C_4H_7O		p.w., [98]**	-44.08	333.01	97.89	120.74	141.00	158.51	184.59	201.21	229.83
			[94]	-59.73	333.56	111.02	133.22	151.48	166.45	189.52	206.78	234.25
DF				***15.65***	***0.56***	***13.13***	***12.48***	***10.48***	***7.94***	***4.93***	***5.57***	***4.41***

*: predicted values **: used as estimation reference data *a*: RMG_*DFT-QCI-thermo* (RMG sub-category: *DFT-QCI-thermo*) *b*: RMG_*CBS-QB3*-1dHR
c: Mean Absolute Deviation *d*: RMG_*Group Additivity* *e*: Difference with literature data *f*: RMG_*Curran-pentane species* *g*: RMG_*USC-Mech2*

Table 3.8 Comparison of the calculated thermodynamic values and literature data for selected species containing certain ring correction groups [83].

Group	Formula	Molecule	Ref	ΔH_f^0 / kJ·mol^{-1}	S^0 / J·mol^{-1}·K^{-1}	$C_p(T,K)$ /J·mol^{-1}·K^{-1}						
						300	**400**	**500**	**600**	**800**	**1000**	**1500**
RC1	C_3H_6O	 Methyl oxirane	p.w.[*]	-91.07	285.11	71.97	93.94	112.90	128.80	151.87	169.77	202.69
			[106][a], [82]	-92.77	281.43	72.64	92.56	110.78	126.57	149.77	167.09	192.27
			[106] [b]	-88.46	272.74	78.64	97.51	114.48	129.64	154.14	176.62	210.62
			[86]	-93.21	286.33	72.73	92.38	109.93	124.98	148.39	165.53	191.86
			[81]	-94.68	287.40	72.92	92.99	110.99	126.16	149.68	166.85	193.06
MAD [c]				***2.13***	***5.33***	***2.45***	***1.90***	***1.65***	***1.73***	***2.02***	***3.97***	***7.43***
RC2	C_4H_6O	 3-methylene Oxetane	p.w.	18.56	290.90	74.57	100.35	123.44	142.91	170.06	191.04	226.41
			[106] [a]	4.26	290.80	77.68	102.28	122.82	140.29	167.67	187.36	216.58
			[106] [b]	23.91	301.90	75.91	99.79	121.88	141.26	169.87	188.55	219.67
MAD				***8.30***	***5.21***	***1.27***	***1.07***	***0.64***	***1.08***	***1.09***	***1.54***	***4.10***
RC2	C_3H_6O	 oxetane	p.w., [82][**]	-81.11	274.97	61.82	82.56	102.91	120.90	146.60	166.68	203.57
			[106] [a]	-81.09	274.62	61.79	82.56	102.91	120.90	146.60	165.70	193.07
			[106] [d]	-75.05	265.60	61.37	83.10	102.85	120.44	148.21	167.86	200.57
			[81]	-80.54	-	61.94	83.97	104.24	121.31	147.44	166.12	193.93
			[86]	-79.42	274.21	63.54	85.27	105.34	122.47	148.39	166.78	194.79
			[106] [b]	-82.81	272.49	70.60	88.28	107.68	124.69	149.69	168.45	212.51
			[101]	-105.34	270.78	61.95	84.73	105.34	122.35	147.89	165.99	193.28
MAD				***8.56***	***3.01***	***3.74***	***2.18***	***1.88***	***1.57***	***1.12***	***1.04***	***7.75***
RC6	cyC_7H_{14}	 Methyl-cyclohexane	p.w.	-154.83	334.56	126.98	177.53	223.29	263.28	323.83	366.65	427.42
			[106] [b]	-153.42	340.49	134.52	183.95	229.45	269.78	331.03	370.01	430.51
			[81]	-154.80	343.30	136.70	186.0	229.90	266.80	323.50	364.10	424.50
			[91]	-143.0	-	-	-	-	-	-	-	-
MAD				***4.95***	***3.64***	***4.16***	***3.61***	***3.01***	***2.66***	***3.47***	***2.42***	***2.45***
RC7	cyC_6H_{10}	 Cyclohexene	p.w., [81][**]	-4.37	310.31	102.16	139.77	173.10	201.59	244.61	275.32	321.55
			[82]	-4.61	310.56	101.40	138.69	172.75	202.12	244.76	276.05	320.30
			[91]	7.20	-	-	-	-	-	-	-	-
MAD				***5.56***	***-***	***-***	***-***	***-***	***-***	***-***	***-***	***-***
DF [e]				***0.04***	***0.94***	***0.04***	***1.08***	***0.34***	***0.53***	***0.16***	***0.73***	***1.25***

RC6	$cyC_6H_{10}O$	 d-$cyC_6H_{10}O$	p.w.	-239.27	331.32	111.48	152.36	187.40	218.16	268.12	301.86	358.53
			[106] [b]	-231.67	340.55	122.39	160.54	194.89	224.86	270.01	299.79	340.39
			[106] [d]	-225.68	334.52	120.55	159.81	195.22	226.07	271.84	299.98	352.91
			[81]	-231.1	335.53	121.89	161.88	196.39	225.24	269.47	301.06	-
MAD				***4.84***	***3.32***	***4.44***	***3.71***	***3.55***	***3.16***	***1.33***	***0.84***	***7.58***
RC7	cyC_7H_9	 Methylene cyclohexenyl	p.w.	186.38	326.71	110.44	152.65	188.52	217.93	259.05	290.77	334.01
			[106] [f]	196.47	338.17	113.90	152.72	186.63	214.86	254.01	281.44	324.51
DF				***10.09***	***11.46***	***3.47***	***0.07***	***1.89***	***3.07***	***5.04***	***9.33***	***9.49***
RC8	cyC_6H_8	 1,3-Cyclohexadiene	p.w., [82] [**]	106.47	303.32	94.12	127.57	157.54	182.93	218.85	244.92	281.34
			[106] [b]	104.59	296.65	93.49	127.17	157.26	182.56	217.73	243.12	281.52
			[106] [g]	106.20	303.19	93.60	126.75	157.18	183.48	220.63	242.76	286.92
			[81]	104.58	-	94.8	128.55	157.99	182.24	218.7	244.45	282.52
			[91]	120.2								
MAD				***5.95***	***3.11***	***0.53***	***0.58***	***0.30***	***0.28***	***0.50***	***0.76***	***0.52***

*: present work *f*: RMG, vinylCPD_H **: used as estimation reference data *g*: RMG_*CH* (RMG database; sub-category of *CH*) *c*: Mean Absolute Deviation
b: RMG_*Group Additivity* *e*: Difference with literature data *a*: RMG_*Curran-pentane species* *d*: RMG_*CHO*

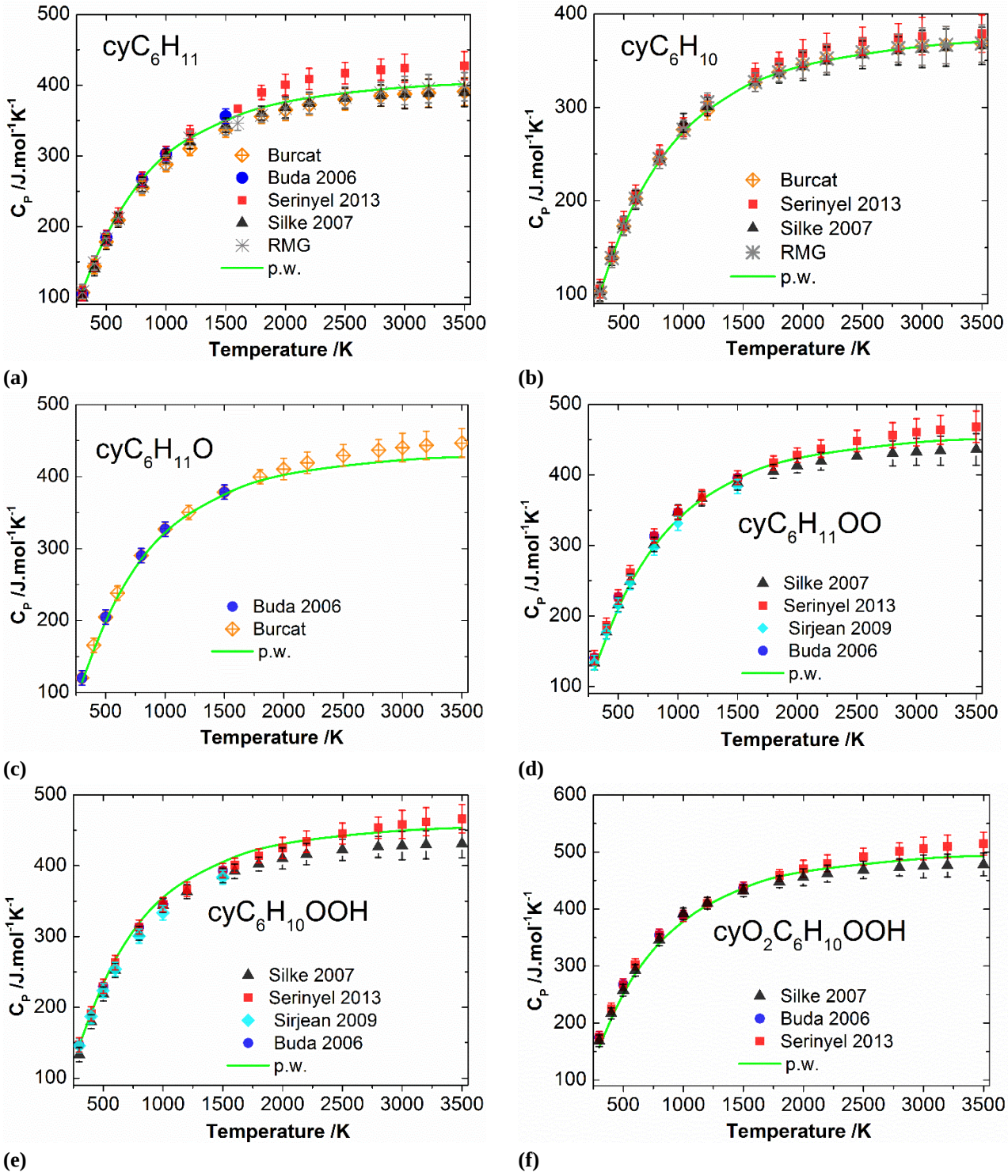


Figure 3.2 Predicted values of heat capacity (solid lines) compared to data from kinetic models and databases [9, 29, 30, 48, 49, 81, 82, 106] (symbols). *Note: Also published in* [83].

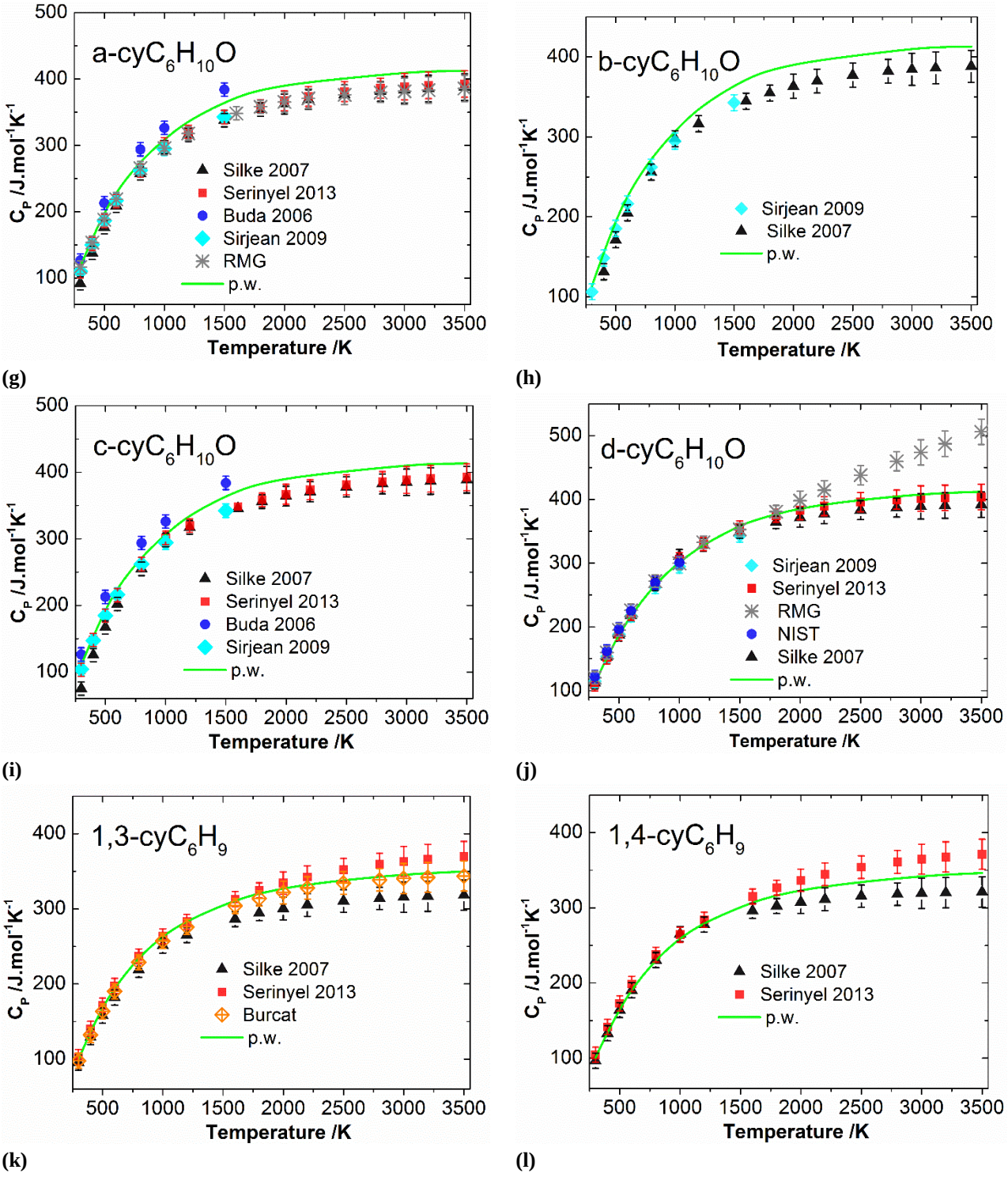


Figure 3.2 *Continued* - Predicted values of heat capacity (solid lines) compared to data from kinetic models and databases [9, 29, 30, 48, 49, 81, 82, 106] (symbols). *Note: Also published in* [83].

The presented species vary from each other in structure and functional groups, including linear and cyclic alkanes, radicals and oxygenated compounds. It can be seen that, there is a good consistency between literatures data and predictions. In most cases, the heat capacity values, estimated in the present work were predicted to be close to the average of the available literature data. The maximum deviation occurs for cy$C_6H_{10}O$ around 20 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, i.e. at a 5% lower value than used by model of Serinyel et al. [30] at 3500 K, see Fig 3.2c. The estimated uncertainty intervals for literature data, DF and MAD, are provided in Tables 3.7-8. They were under 10.00 $J{\cdot}mol^{-1}{\cdot}K^{-1}$ for the range 300-2000 K. The uncertainty of calculations rises with increasing temperature; uncertainty intervals increase to 15 $J{\cdot}mol^{-1}{\cdot}K^{-1}$ for the range 2000-3000 K and to 20 $J{\cdot}mol^{-1}{\cdot}K^{-1}$ above 3000 K.

Table 3.9 provides the results of performed calculations. Also, for the aim of comparison, the literature data from well-established cyclohexane modelling studies, from the NIST [81], Burcat [82] and RMG database [106] have been presented in Table 3.9. As expected in the case of well-studied species, the method used in this work delivers good agreement with the other models. Unlike the heat capacities (Fig 3.2a-l), the deviations increase as the intermediates become more complex in structure. For the case of bicyclic ethers a,b,c-cy$C_6H_{10}O$, high *MAD* values have been obtained for both ΔH_f^0 and S^0.

Table 3.9 Comparison between properties values predicted and used in other cyclohexane models, NIST [81] and Burcat [82] databases.

Species	**p.w.***		**Silke et al. [9]**		**Buda et al. [29]**		**Serinyel et al. [30]**		**Sirjean et al. [49, 48]**		**NIST [81], Burcat [82]**		**RMG [106]**		***MAD*****	
	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0
cyC_6H_{11}	50.85	311.87	70.35	326.81	74.70	317.93	71.22	318.95	71.48	325.2	75.82[b]	317.75[b]	71.12	325.48	7.79	5.04
cyC_6H_{10}	-4.57	309.63	-4.62	316.23	-	-	-5.73	310.68	-0.41	304.3	-4.32[a]	310.45[a]	-4.61	310.56	1.69	3.46
cy$C_6H_{11}O$	-72.09	328.48	-	-	-71.48	314.46	-71.56	314.74	-	-	-	-	-	-	0.27	6.54
cy$C_6H_{11}OO$	-86.93	362.08	-87.18	378.94	-81.26	370.89	-84.21	371.25	-93.21	366.59	-	-	-	-	3.96	5.60
cy$C_6H_{10}OOH$-1	-25.83	385.30	-31.99	402.33	-29.84	400.53	-36.22	401.92	-18.39	380.80	-	-	-	-	6.05	9.21
cy$OOC_6H_{10}OOH$	-183.78	438.26	-190.32	449.34	-183.08	453.03	-185.08	453.48	-	-	-	-	-	-	2.84	6.14
cyOC_6H_9OOH	-335.83	408.48	-339.65	409.62	-	-	-353.12	377.49	-	-	-	-	-	-	7.42	14.88
a-cy$C_6H_{10}O$	-128.14	283.15	-30.52	272.51	-118.09	312.7	-126.80	322.97	-126.65	322.70	-125.52[a]	-	-76.36[c]	329.37[c]	34.72	21.57
b-cy$C_6H_{10}O$	-135.77	257.77	-37.80	261.93	-	-	-	-	-107.00	316.43	-	-	-	-	41.12	26.73
c-cy$C_6H_{10}O$	-218.09	227.37	-121.6	253.44	-177.44	312.71	-183.28	313.34	-183.08	313.08	-	-	-	-	31.09	36.53
d-cy$C_6H_{10}O$	-239.27	331.32	-236.80	338.24	-	-	-230.52	322.10	-232.83	334.82	-231.10[a]	335.53[a]	-225.68 [d]	334.52 [d]	4.41	5.18
cyC_6H_9-1,3	121.44	303.71	106.50	309.67	-	-	126.92	321.35	-	-	131.45[b]	313.65[b]			9.40	6.41
cyC_6H_9-1,4	184.61	318.49	109.18	291.06	-	-	192.81	322.32	-	-	-	-	-	-	37.64	13.92

ΔH_f^0 , S^0 are in $kJ{\cdot}mol^{-1}$ and $J{\cdot}mol^{-1}{\cdot}K^{-1}$, *respectively.*

*: present work **: Mean Absolute Deviation *a*: NIST [81] *b*: Burcat [82] *c*: RMG_*Group Additivity* (RMG database; sub-category: *Group Additivity*) *d*: RMG_*CHO*

3.4.2. Benson Groups and NASA Coefficients of Low Temperature Species

The "THERM-PLY" code, developed at DLR (German Aerospace Center), Stuttgart, which estimates the thermodynamic properties of species based on the Benson Additivity Group, was used to approximate $\Delta H_f^0, S^0, C_p(T)$ and the corresponding NASA polynomial coefficients of the species, occurring in current cyclohexane sub-mechanism.

The inputs of this program are the list of Benson groups, and configuration information (linearity and symmetry). The outputs present the estimated values within T=300-1500 K, the extrapolation of the properties up to 3500 K, and the corresponding NASA polynomial coefficients. The "THERM-PLY" code implements the FUMILI tool [69, 70, 71] for approximation and calculation of the NASA coefficients. The first 7 series of coefficients (a_1-a_7) stand for the high temperature zone, the next 7 coefficients (a_8-a_{14}) correspond to the low temperature, and the last value (a_{15}) represents $\Delta H_f^0 / R$ (mol·K^{-1}). Table A.1 in *Appendix V* lists these values for select species important to the low temperature reaction mechanism of cyclohexane. Table 3.10 summarizes the calculated thermodynamic data for relevant intermediate species in current cyclohexane sub-mechanism.

Table 3.10 Calculated thermodynamic properties of cyclohexane relevant sub-model species.

Species	ΔH_f^0 / kJ·mol^{-1}	S^0 / J·mol^{-1}·K^{-1}	$C_p(T)$ /J·mol^{-1}·K^{-1}						
			300	**400**	**500**	**600**	**800**	**1000**	**1500**
cyC$_6$H$_{11}$	50.85	311.87	103.83	145.13	182.47	215.21	265.16	299.71	347.83
cyC$_6$H$_{10}$	-4.57	309.63	101.37	139.77	173.10	201.59	244.61	275.32	321.55
cyC$_6$H$_{11}$O	-72.09	328.48	113.50	159.00	199.19	234.26	288.20	323.54	377.42
cyC$_6$H$_{11}$OO	-86.93	362.08	123.33	169.37	211.06	247.25	300.98	338.09	397.01
cyC$_6$H$_{10}$OOH	-25.83	385.30	143.39	186.66	224.80	257.71	308.04	339.12	387.77
cyC$_6$H$_{10}$OOH (Lump)	-43.95	393.46	144.67	192.81	233.81	268.81	322.07	356.55	407.34
cyOOC$_6$H$_{10}$OOH	-183.78	438.26	157.34	208.06	251.58	288.47	343.09	379.00	439.26
cyOOHC$_6$H$_9$OOH	-122.33	446.94	178.57	229.62	271.44	306.82	361.45	392.85	443.80
cyOC$_6$H$_9$OOH	-335.83	408.48	146.48	191.03	227.93	259.38	310.21	342.78	400.68
cyC$_6$H$_9$OO	33.38	371.06	119.45	160.45	195.65	225.27	268.60	299.00	351.66
cyC$_6$H$_8$OOH	107.44	384.53	138.45	175.67	207.35	234.23	274.36	299.30	342.19
a-cyC$_6$H$_{10}$O	-128.14	283.15	116.45	159.57	197.90	230.17	276.50	308.81	366.99
b-cyC$_6$H$_{10}$O	-135.77	257.77	113.62	155.54	194.48	227.64	274.00	307.00	366.56
c-cyC$_6$H$_{10}$O	-218.09	227.37	110.44	153.55	193.22	226.76	273.33	306.62	366.39
d-cyC$_6$H$_{10}$O	-239.27	331.32	110.60	152.33	187.47	218.10	268.14	301.85	358.60
cyC$_6$H$_9$O (Lump)	47.59	294.37	115.00	156.00	191.87	221.80	264.67	294.12	347.90
cyC$_6$H$_9$	121.44	303.71	99.08	136.61	168.39	195.25	235.73	263.97	306.29
cyC$_6$H$_8$	106.47	303.32	94.12	127.57	157.54	182.93	218.85	244.92	281.34
cyC$_6$H$_7$	200.56	305.77	97.56	129.46	156.63	178.98	210.14	232.58	263.86

4. Determination of Transport Properties

4.1. Introduction

Species transport properties are known as one of the important factors in determination of the state of the fluids and play an important role in simulation of the premixed- as well as diffusion flames [112]. Estimation of transport properties of species in gaseous mixtures requires the evaluation of diffusion coefficients, viscosities, thermal conductivities and thermal diffusion coefficients. There are various possibilities for evaluating mixture properties [113]. However, computing the mixture properties can be expensive and it is often recommended to reduce the computational cost. Moreover, there are some applications in which the approximate averaging rules are not adequate.

The TRANSPORT property program, used as a part of the CHEMKIN Collections [113], is based on the work of Dixon-Lewis [113, 114] and the methods for mixture-averaged approach, reported in Warnatz [115] and Kee et al. [116]. For species occurring in reaction mechanism, six main parameters, namely: Molecular parameters, the Lennard-Jones potential well-depth, Lennard-Jones collision diameter, dipole-moment, polarizability, and rotational relaxation (collision) number at 300 K, are required as input for CHEMKIN calculations. Coming up with estimations of these parameters, the transport database can be extended for new species occurring in the current kinetic reaction model. In the following sections these key transport parameters and their estimation methods will be discussed.

4.2. Main Transport Input Parameters

4.2.1. Molecular Parameters

This parameter characterizes the geometrical configuration and is identified by digits "0, 1, 2" in the CHEMKIN input file. The Index "0" shows a single atom, index "1" indicates linear configuration and the index "2" indicates the nonlinear structure.

4.2.2. The Lennard-Jones Potential, Well Depth and Diameter

The Lennard-Jones potential $\varphi(r)$ describes the energy of interactions between molecules. The well depth factor is a measure which indicates the strength of the interaction. The Lennard-Jones (L-J) potential is a function of distance between molecules and correlates with the well depth as follows [117, 118]:

$$\varphi(r) = 4\varepsilon \cdot \left[\left(\frac{\sigma}{r_d}\right)^{12} - \left(\frac{\sigma}{r_d}\right)^{6}\right] \qquad Eq\ (4.1)$$

where ε represents the L-J well depth, r_d is the separation distance (in Å= 10^{-10} m) between two particles, and σ is the L-J collision diameter (also in Å), which is in fact the distance of zero intermolecular interaction potential. The estimation of the well depth and diameter follows from the correlations with acentric factor ω, and critical properties of the species, specifically critical temperature T_c (in K), and critical pressure P_c (bar) [118]:

$$\frac{\varepsilon}{k_b \cdot T_c} = 0.7915 + 0.1693\omega \quad , \quad \sigma\left(\frac{P_c}{T_c}\right)^{1/3} = 2.3551 + 0.087\omega \qquad Eq\ (4.2)$$

where k_b is the Boltzmann's constant. The acentric factor is a commonly used constant, which is derived from an experimental vapour pressure temperature function. The monatomic gases (Ar, Kr, Xe) have $\omega \cong 0$ and except for quantum gases (H_2, He, Ne) and a few others (for instance Rn), all other species have positive values of ω up to 1.5 [118]. As defined by Pitzer, et al. 1955 [119] the acentric factor is originated from the following correlation:

$$\omega \equiv \log[\lim_{T/T_c \to 0.7}(P_{vp}/P_c)] - 1.0 \qquad Eq\ (4.3)$$

where the term P_{vp} represents the vapor pressure. The convenient method to estimate the acentric factor is via the critical constants such as T_c , P_c and using one or more experimentally (or empirically) determination of the properties such as boiling temperature T_b [118]:

$$\omega = \frac{-\ln(P_c) - 5.927 + 6.096{T_r}^{-1} + 1.289\ln(T_r) - 0.169{T_r}^{6}}{15.252 - 15.688{T_r}^{-1} - 13.472\ln(T_r) + 0.436{T_r}^{6}} \qquad Eq\ (4.4)$$

where T_r is the dimensionless temperature defined as: $T_r = T_b/T_c$. For the cyclohexane sub-model species, the critical properties can be calculated using additivity rules (see section 4.3). Then the acentric factor, L-J well-depth and collision diameters will be evaluated (see section 4.4, Table 4.2).

4.2.3. The Dipole Moment

The dipole moment μ of a molecule is often required for estimation of properties such as virial coefficients and viscosities [118]. The unit of μ is Debye (1D=3.333·10^{-10} C·m [coulomb meter]). Normally the values for dipole moments do not vary with temperature and the difference between gas and liquid phase values is normally neglected. The dipole is often used to indicate whether electrostatic contributions are significant compared to van der Waals attraction [118]. By definition, the dipole moment vector points from the centre of the positive charge distribution to the centre of the negative charge distribution [120]. Therefore, the electric dipole moment is highly dependent on the geometry of species. As an example, methane and ethane molecules are known as nonpolar due to their symmetrical configurations, and the bonds between equivalent atoms. Therefore, their dipole moments are considered as zero. Based on the principle of bond moments, the moment for the CH_3 group equals with one C-H moment, which means that the substitution of the aliphatic H by CH_3 group does not change the dipole moment. Therefore, all saturated hydrocarbons have zero moments as long as they keep the tetrahedral geometry at each C-atom [121]. To put it into a general way, depending on the substitutions of X within the C-X configuration, the dipole moment of the group changes proportional to the difference in electronegativity between C and X-atom.

4.2.4. The Electronic Polarizability

The polarizability of a molecule α ($Å^3$ =10^{-24} m) is one of the important electrical aspects of species and mixtures. It indicates the tendency of a molecule to be distorted in the presence of an

electric field. It is mainly dependent on the strength of the nuclear force, controlling the electrons and preventing their distortion by the applied field [122]. The polarizability can be experimentally determined via strength of the electric field, dipole moments, and dielectric constants. It correlates with the magnitude of the externally exposed electric field, and the electric dipole moments [122]:

$$\mu = \alpha \cdot \epsilon \qquad Eq\ (4.5)$$

where μ is the dipole moment in unit Debye (D) and ϵ represents the magnitude of the electric field in $N \cdot C^{-1}$. Similar to other thermo-physical terms, quantum mechanical calculations can be used to evaluate the molecular polarizability based on force constants, bond lengths and frequencies. An estimation modus has been developed by Stout et al. [123] which is derived from ab-initio calculations over 30 molecules and containing up to four non-hydrogen (C, N, O, and F) atoms. Kier and Hall [124, 125] proposed a model based on the Quantitative Structure-Property Relationship (QSPR) approach, for the molar refraction of alkanes and certain aliphatic derivatives [122]. The QSPR approach was further implied by [126-128] to study the refractive indexes of organic compounds and polymers. However, due to the numerous calculations which were required in the case of the species occurring in current sub-model, and considering time and cost of each quantum mechanical calculations, empirical estimations were preferred.

Partington [129] revealed the additive specification for polarizability of a molecule and showed that, it can be approximated through summing up the polarizability of each contribution. The additivity approaches were later developed by Applequist et al. [130] based on the tensor treatments and an idea that, addition of each group tensor yields the overall molecular polarizability tensor. Bosque et al. [122] developed an additivity modus for average polarizability of solvents via a set of atomic polarizabilities within the molecules for C, H, O, S, N, P, F, Cl, Br, and I. Their method was validated over large sets of solvents, including 426 different chemical compounds, such as cyclic and acyclic nonaromatic hydrocarbons, aromatic hydrocarbons, halogenated compounds, alcohols, ethers esters, aldehydes, and ketones.

The additivity model was derived from fitting the experimental values of α with the number of atoms of each element present in the molecule. The proposed model allows the calculation of the polarizability from the number of atoms of each element (for example: number of carbon atoms #C, number of hydrogen atoms #H, and number of oxygen atoms #O) presented in the composition of the compounds. Thus, "the average atomic polarizability" in fact applies to each element separately regardless of its chemical and structural characteristics [122]:

$$\alpha = 1.51(\#\mathrm{C}) + 0.17(\#\mathrm{H}) + 0.57(\#\mathrm{O}) + 1.05(\#\mathrm{N}) + 2.99(\#\mathrm{S}) + 2.48(\#\mathrm{P}) + 0.22(\#\mathrm{F}) + 2.16(\#\mathrm{Cl}) + 3.29(\#\mathrm{Br}) + 5.45(\#\mathrm{I}) + 0.32 \qquad Eq\ (4.6)$$

The accuracy of this empirical correlation was assured by testing over the coefficient regression, as well as calculation of standard deviation, the relative standard deviation from experimental values, and the average absolute and relative error. Unlike the classic additive methods, this method does not consider the structural units, for instance, presence of double and triple bonds. However, it delivers an acceptable level of uncertainties and showed consistency with the experimentally determined values [122].

4.2.5. The Rotational Relaxation Number

The rotational relaxation collision number Z_{rot} is dependent on geometrical parameters and temperature, as shown in [131, 132]. Therefore, it is normally assumed at standard temperature, T= 298 K. According to [133, 134], the $Z_{rot}(298\ K)$ can be expressed by following empirical correlation:

$$Z_{rot}(298\ K) = \frac{3}{8}\frac{(1+b)^2}{b}\ ,\ b = \frac{I_m}{\mu_m \cdot d^2} \qquad Eq\ (4.7)$$

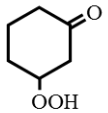
where I (kg·m^2) is the total internal moment of inertia of the molecule, μ_m (kg) is the reduced collision mass between two particles ($\mu_m = m_x m_y/(m_x + m_y)$), and d represents the diameter of the molecule (μm). The total internal axial moment of inertia is calculated by each axial contribution of inertia:

$$I_m = [I_x \cdot I_y \cdot I_z]^{1/2} \qquad Eq\ (4.8)$$

4.3. Evaluation of Boiling and Critical Properties of Species

The additive group contribution method by Joback and Reid [99] was utilized to determine the boiling temperatureT_b, the critical temperatureT_c, and the critical pressure P_c of the new species. These parameters are the prerequisites for estimation of L-J parameter, see *Eq* (4.2-4.4). Joback and Reid [99] developed a mathematical-empirical modus for each physical property, based on the additive treatment of constructive group contributions; see Table II of [99]. It has to be mentioned that, this is a first-order approximation and does not consider any interaction between the group contributions, since there was not adequate reliable data on "next-nearest neighbours" interactions. These group contributions are available in Table III of [99]. To have a better understanding about the calculation procedure, one of the intermediates in low temperature sub-model, the cyOC$_6$H$_9$OOH molecule, is considered as an example. The properties of this molecule can be described by its group contributions, i.e.: "–CH2–", ">CH–" from ring carbon increments, ">C=O" from oxygen ring increments, and "–O–", "–OH" from oxygen non-ring increments collection (Table III of [99]), see Table 4.1.

Table 4.1 Estimation of boiling and critical properties of cyclic ketohydroperoxy cyOC$_6$H$_9$OOH, using Joback and Reid additivity method [99].

Molecule	**Joback& Reid Contribution Groups**	**No.**	T_b/ K *	T_c/ K **	P_c/ bar ***
	–CH$_2$– (ring)	4	21.15	0.0100	0.0025
	>C=O (ring)	1	94.97	0.0284	0.0028
	>CH– (ring)	1	21.78	0.0122	0.0004
	–O– (non-ring)	1	22.42	0.0168	0.0015
#Atoms: n$_A$=19					
M = 130 g	–OH (alcohol)	1	92.88	0.0741	0.0112
cyOC$_6$H$_9$OOH			***514.85***	***714.98***	***45.72***

Note: *T_b=198.2+Σ($T_{b,i}$) ** T_c= T_b [0.584+0.965·Σ($T_{c,i}$)-(Σ($T_{c,i}$))^2]$^{-1}$ *** P_c=[0.113+0.0032 n_A - Σ($P_{c,i}$)]$^{-2}$

4.4. Approximation of Key Transport Properties

Determination of the boiling and critical physical properties, i.e.$T_b, T_c,$ and P_c enables us with evaluation of acentric factor ω (*Eq* (4.4)), L-J well-depth ε, and the collision diameter σ (*Eq* (4.2)) for all occurring species in the sub-model. The polarizability values were estimated by the mathematical correlation of *Eq* (4.6). Since the dipole moment is strongly dependent on geometrical specifications and distribution of electronegativity, they were set after comparison with the species, with similar functional groups and geometry, available in other sub-models in the kinetic mechanism.

The same strategy has been applied for determination of rotational relaxation number $Z_{rot}(298\ K)$, regarding its reliance on structural and geometrical parameters, mass and size of the molecules, see *Eq* (4.7). Table 4.2 summarizes these approximations for species of cyclohexane sub-mechanism. Also, the transport data input file in *Appendix III* contains these parameters in required CHEMKIN format for running simulations.

Table 4.2 Main transport properties of cyclohexane relevant sub-model species, estimated in current study.

Species	T_b/ *K*	T_c/ *K*	P_c/ *bar*	ω/-	σ/ *A*	ε/ *K*	α/A^3	μ/*D*	Z_{rot}/-
cyC_6H_{12}	325.10	509.32	41.30	0.212	5.398	421.38	11.42	0.61	2.6
cyC_6H_{11}	325.10	509.32	43.06	0.225	5.321	422.49	11.25	0.61	2.6
cyC_6H_{10}	336.26	529.34	43.28	0.210	5.384	437.82	11.08	0.55	2.7
$cyC_6H_{11}O$	348.15	532.34	40.99	0.295	5.475	447.95	11.76	0.61	2.6
$cyC_6H_{11}OO$	370.57	555.35	40.11	0.368	5.578	474.16	12.27	2.9	1.9
$cyC_6H_{10}OOH$	441.03	622.66	45.53	0.731	5.479	569.89	12.44	0.55	1.4
$cyOOC_6H_{10}OOH$	486.50	665.89	42.33	0.913	5.701	630.03	13.29	3.08	1.8
$cyOOHC_6H_9OOH$	556.96	731.91	48.23	1.361	5.536	747.99	13.29	3.08	1.8
$cyOC_6H_9OOH$	514.85	714.98	45.72	0.844	5.705	668.12	12.61	0.6	1.4
cyC_6H_9OO	381.73	574.49	42.00	0.367	5.556	490.38	11.93	2.9	1.9
cyC_6H_8OOH	452.19	640.57	47.83	0.732	5.441	586.37	11.93	0.55	1.4
a,b,c-$cyC_6H_{10}O$	357.58	550.04	43.40	0.292	5.432	462.52	11.59	1.74	2.7
d-$cyC_6H_{10}O$	398.92	610.43	43.23	0.310	5.627	515.20	11.59	1.74	2.7
cyC_6H_9O (Lump)	357.58	550.04	45.29	0.306	5.352	463.82	11.42	0.4	2.7
cyC_6H_9	336.26	529.34	45.16	0.223	5.305	438.97	10.91	0.2	2.7
cyC_6H_8	347.42	549.57	45.41	0.222	5.285	455.63	12.27	0.44	2.7
cyC_6H_7	347.42	549.57	47.43	0.368	5.578	474.16	13.29	0.44	2.7

5. Results of the Cyclohexane Kinetic Model and Discussions

5.1. Review of Available Experimental Data

The performance of the current cyclohexane model was validated against a wide range of experimental data, namely ignition delay times data measured in Rapid Compression Machines (RCM) [31, 38] and shock tubes (ST) [27, 37, 42] at low and high temperatures and pressures, laminar flame speed data [32, 35, 36, 30, 41] at 300 K at pressure of 1 atm, and elevated pressures. The PAH precursor concentrations, measured in laminar premixed cyclohexane flames [33, 34, 40] were also investigated by current model. Table 3.1 summarizes these experiments alongside with their conditions, used for validation.

Table 5.1 Experimental data used for validations (ST: Shock tube, RCM: Rapid Compression FL: Flame structure MFR: Mass Flow Rate).

Exp.	Validation		
	ST	**RCM**	**FL**
Law et al. [33, 34]			**Concentration profile** **T** = 1000 K, **p** = 30 Torr, **φ** = 1.0 **Mixture:** cyC_6H_{12}/O_2 in 32.5% Ar **MFR**=0.00214 $g{\cdot}cm^{-2}{\cdot}s^{-1}$
Vranckx et al. [38]		**Ignition delay time** **T** = 600-900 K, **φ** = 1.0, **p** = 20 bar **Mixture:** 2.26% $cyC_6H_{12}/O_2/N_2$	
Lemaire et al. [31]		**Ignition delay time** **p** = 8 bar, **T** = 650-900 K , **φ**=1.0 **Mixture:** cyC_6H_{12}/ air	
Sirjean et al. [27]	**Ignition delay time** **T** = 1230-1840 K, **p** = 8atm , **φ** = 0.5, 2.0 **Mixture:** 0.5% cyC_6H_{12}/O_2/Ar		
Ciajolo et al. [40]			**Concentration profile** **T** = 700 K, **p** = 1 atm, **φ** = 2.33 **Mixture:** cyC_6H_{12}/O_2/39.4% N_2 **MFR** = 0.00283 $g{\cdot}cm^{-2}{\cdot}s^{-1}$
Richter et al. [41]			**Flame Speed** **T** = 473 K, **p** = 1 atm **Mixture:** cyC_6H_{12}/ air
Naumann et al. [42]	**Ignition delay time** **T** = 800-1400 K, **p** = 16atm, **φ** =1.0 **Mixture:** cyC_6H_{12}/O_2/ 89% N_2		
Daley et al. [37]	**Ignition delay time** **T** = 950-1200 K **p** = 13-15 bar, **φ** = 0.25, 0.5, 1.0 **Mixture:** cyC_6H_{12}/ air		
Davis et al. [32]			**Flame Speed** **T** = 298 K, **p** = 1atm **Mixture:** cyC_6H_{12}/ air
Wu et al. [36]			**Flame Speed** **T** = 353 K, **p** = 1.0, 10 atm **Mixture:** cyC_6H_{12}/ air
Ji et al. [35]			**Flame Speed** **T** = 353 K , **p** = 1.0 atm **Mixture:** cyC_6H_{12}/ air
Serinyel et al. [30]			**Flame Speed** **T** = 358 K, **p** = 1atm, **Mixture:** cyC_6H_{12}/ air

5.2. Validation on Experimental Data

5.2.1. Uncertainty of Experimental Data Used for Validation

The uncertainty evaluation of experimental ignition delay data and laminar flame speed data is influenced by many "non-ideality", which was widely discussed in details by Slavinskaya et al. [17]. For example, regarding shock-tube experiments, the main non-ideality were due to the gas-dynamics effects, specifically the boundary layer formation after shock passing, which creates hydro- and thermo- non-homogeneous conditions behind the shock-wave, and the aftershock compression resulting from the interaction of the reflected shock-wave with the contact surface [17]. Therefore, factors and parameters such as operating conditions, length and diameter of the driven section, duration of the reaction, mixture dilution, the nature of carrier gas (CG), and all other factors, which can potentially affect the shock-wave phenomena, are decisive in determination of experimental uncertainty. However, these factors are mostly ignored in approximation of the data uncertainty intervals, claimed by the experimental studies.

In the case of the flame speed data, the minimum uncertainties increments were assumed to be around 10 % and they are defined at around p = 1-5 atm, φ = 0.5 - 1.0, where the diagram of laminar flame speed (S_l) versus equivalent ratio (φ) hits the maximum. The uncertainty increases as the pressure elevates and the mixture becomes richer. The proposed algorithms for uncertainty intervals evaluation, which were discussed in [17], have been also applied in this work (see Tables 2-3 of [17]).

5.2.2. Implementation of the Rate Constant Coefficients

Based on the mechanism analysis and experimental data simulations with previous mechanism of Abbasi et al. [55], certain reaction paths were newly introduced in the mechanism and the reaction rate parameters for several reactions were modified.

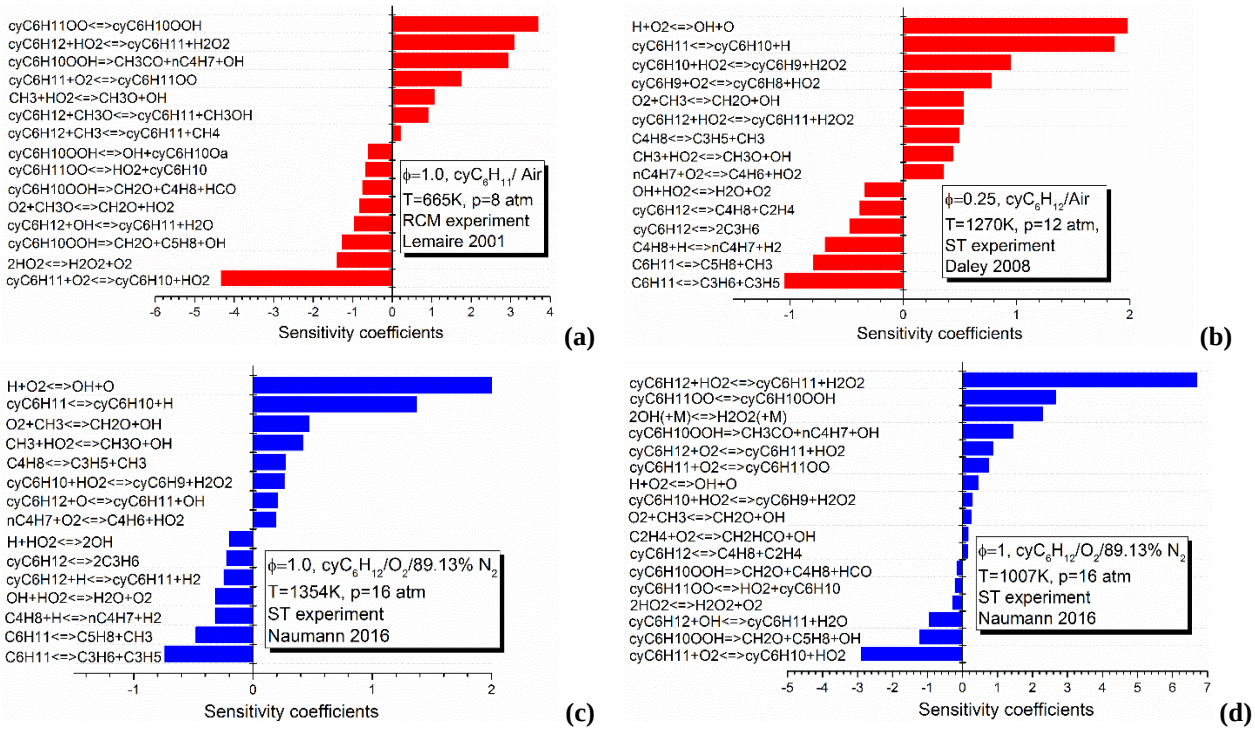


Figure 5.1 Sensitivity coefficients of the OH concentration to reactions in: a) φ = 1.0, T = 665 K and p = 8 atm from RCM experiment [31], b) φ = 0.25, T = 1270 K and p = 12 atm from ST experiment [37], c) φ =1.0, T = 1354 K and p = 16 atm from ST experiment [42], d) φ=1.0, T = 1007 K and p = 16 atm from ST experiment [42].

The sensitivity analyses with respect to the OH radical concentration were carried out based on the performance of our previous kinetic model of Abbasi et al. [55] on four different ignition delay experimental points (Fig 5.1). Fig 5.1a,b present the results obtained for the experimental points (targets), where the response of the model needs to be improved, while the experimental points on Fig 5.1c,d were well reproduced by the our previous model [55].

Based on these results certain reactions were selected for rate modifications. The final list of modifications, alongside with the rate parameters before and after modifications, and the estimated upper and lower uncertainty margins are tabulated in Table 5.2. All performed estimations and modifications remain within the estimated uncertainty intervals (see Section 2.6.2, Fig 2.7.)

Table 5.2 Reaction rate parameters and their estimated lower and upper uncertainty factors for modified reactions.

No.	Reaction*	ΔT, K	Initial rate [55]			Ref.	Modified rate			Ref.	f_l and f_u
			A	β	E_a		A	β	E_a		
R7	$cyC_6H_{12} + O \leftrightarrows cyC_6H_{11} + OH$	500-3000	2.60E+06	2.0	2553	[23]	4.34E+09	1.33	3427.5	*GC* [a]	4.07-4.25
R22	$cyC_6H_{11}+O_2 \leftrightarrows cyC_6H_{10}+HO_2$	700-3000	1.50E+12	0.0	4251.2	[26]	1.17E+13	0.0	7479.7	*EM* [b]	1.68-1.77
R35	$cyC_6H_{10} + H \leftrightarrows cyC_6H_9 + H_2$	500-3000	3.97E+13	0.0	6562	*EM*	6.00E+12	0.0	4445	[22]	2.25-2.56
R37	$cyC_6H_{10}+HO_2 \leftrightarrows cyC_6H_9+H_2O_2$	600-3000	1.14E+13	0.0	10709.5	*EM*	4.49E+10	0.6	15828	*GC*	2.39-2.61
R85	$cyC_6H_{11}OO \leftrightarrows cyC_6H_{10}OOH$	800-3000	1.50E+12	0.0	24076	[15] [c]	2.00E+12	0.0	24045	[22] [d]	3.34-3.82
R89	$cyC_6H_{10}OOH \leftrightarrows OH+cyC_6H_{10}Oa$	700-3000	1.00E+12	0.0	10400	[28]	9.31E+09	0.6	8437.08	*GC*	2.84-3.14
R90	$cyC_6H_{10}OOH \leftrightarrows OH+cyC_6H_{10}Ob$	600-3000	1.50E+12	0.0	23400	[28]	1.25E+10	0.8	21662.2	*GC*	3.51-3.86
R91	$cyC_6H_{10}OOH \leftrightarrows OH+cyC_6H_{10}Oc$	800-3000	1.90E+12	0.0	20700	[28]	1.08E+12	0.6	23692.3	*GC*	2.78-2.97
R97	$cyC_6H_{10}Oa+OH \leftrightarrows cyC_6H_9O+H_2O$	500-3000	3.40E+06	1.9	-1451	[13] [c]	3.71E+12	0.2	1133.5	*GC*	0.88-0.93
R98	$cyC_6H_{10}Oa+HO_2 \leftrightarrows cyC_6H_9O+H_2O_2$	500-3000	4.00E+03	2.5	14300	[13] [c]	1.72E+11	0.5	16376	*GC*	2.36-2.66
R99	$cyC_6H_{10}Oa+H \leftrightarrows cyC_6H_9O+H_2$	500-3000	1.20E+06	2.4	2583	[13] [c]	1.01E+13	0.3	5210	*GC*	1.26-1.36
R100	$cyC_6H_{10}Oa+CH_3 \leftrightarrows cyC_6H_9O+CH_4$	500-3000	1.79E+04	2.33	6147	[13] [c]	2.51E+10	0.53	7524	*GC*	1.67-4.72
R102	$cyC_6H_{10}Ob+HO_2 \leftrightarrows cyC_6H_9O+H_2O_2$	500-3000	4.00E+03	2.5	14300	[13] [c]	1.72E+11	0.5	16376	*GC*	2.55-3.20
R105	$cyC_6H_{10}Oc+OH \leftrightarrows cyC_6H_9O+H_2O$	500-3000	3.40E+06	1.9	-1451	[13] [c]	3.63E+12	0.2	2940	*GC*	0.93-1.00
R106	$cyC_6H_{10}Oc+HO_2 \leftrightarrows cyC_6H_9O+H_2O_2$	500-3000	4.00E+03	2.5	14300	[13] [c]	1.23E+11	0.5	16368	*GC*	2.17-2.36
R107	$cyC_6H_{10}Oc+H \leftrightarrows cyC_6H_9O+H_2$	500-3000	1.20E+06	2.4	2583	[13] [c]	9.53E+12	0.3	7010	*GC*	1.37-1.48
R108	$cyC_6H_{10}Oc+CH_3 \leftrightarrows cyC_6H_9O+CH_4$	500-3000	1.79E+04	2.33	6147	[13] [c]	3.43E+09	0.76	7534	*GC*	1.84-3.76

Notes: ***** Reaction rate constants in cm^3, *mol*, *cal* units, $k = AT^{\beta}exp(E/RT)$ a) *GC:* Generic; determined by uncertainty analysis b) *EM:* Estimated using the empirical method of section 2.5 c) Analogous with C_8 d) The factor *A* multiplied by 2/3

5.2.3. Validation on Ignition Delay Time Data

The simulations of experimental data obtained in the RCMs of Lemaire et al. [31] and Vranckx et al. [38] were performed with current mechanisms and two other well-established cylohexane models, namely from Silke et al. [9] and Serinyel et al. [30] (Fig 5.2).

The simulations revealed that, unlike the mechanisms developed by Silke et al. [9] and Serinyel et al. [30], the previous model of the author (Abbasi et al. [55]) did not reproduce two-stage ignition with NTC behaviour. In order to improve the ability of the model, two additional pathways were included in this mechanism, namely isomerization of $cyOOC_6H_{10}OOH$ through the internal hydrogen transfer yielding the more stable $cyC_6H_9(OOH)_2$ radical (*type XIII*, Fig 2.2), which is known as alternative second isomerization path, and the secondary low temperature cyclohexene (cyC_6H_{10}) oxidation pathways (*type XX*, Fig 2.2).

The second isomerization was included in the recent scheme with the aim of strengthening the chain propagation effects, and to increase the concentrations of less reactive HO_2 and cyclohexanone radicals (through the decomposition of $cyOC_6H_9OOH$), specifically in the intermediate temperature zone (800-1000 K).

The secondary ignition of cyclohexene (cyC_6H_{10}) was also added in the current mechanism, with respect to the recommendation of Buda et al. [29] for the NTC region. Cyclohexene is

mostly produced during the cascading cyclohexane dehydrogenation, and by the HO_2 elimination from cyclohexylperoxy radical. In our new model cyclohexene further decomposes into cyclohexenyl, cyC_6H_9. This can be also viewed as an initial step for the second ignition. The resulted cyC_6H_9 reacts with molecular oxygen and starts the low temperature scheme of the cyclic olefin. This makes the low temperature cyclohexene oxidation path competitive with the low temperature hexyl oxidation.

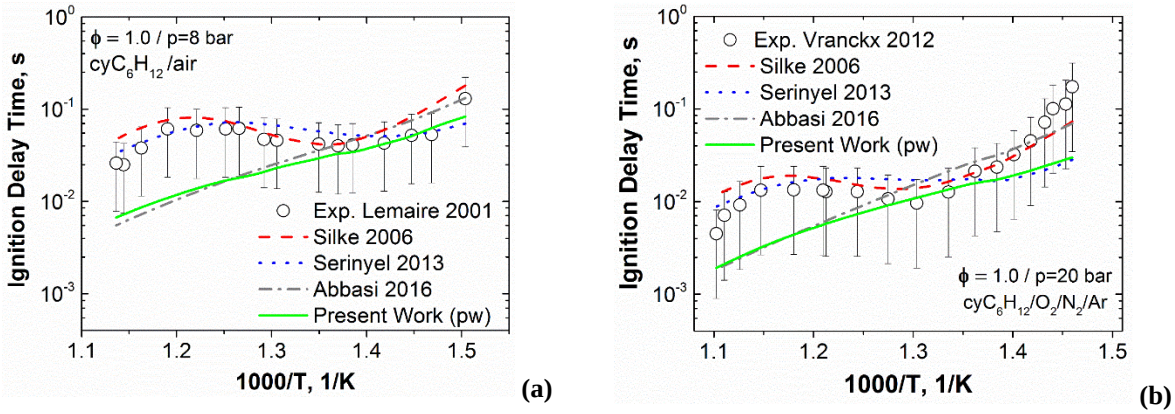


Figure 5.2 Cyclohexane ignition delay time from RCM experiments: a) φ = 1, p = 8 bar [31], b) at φ = 1.0, p = 20 bar [38]. The open symbols and the lines represent the experimental data and the simulations by the models from [9, 30, 55] and presented work (pw), respectively.

It has been observed that, these two additional channels did not remarkably change the trends in the ignition simulations (Fig 5.1). However, compared with the output of our previous model, Abbasi et al. [55], the ignition particularly within the temperature zone of T < 800 K became faster. The reason can be explained due to the additive O–OH bonds, which increase the number of OH radicals, and thus accelerate the fuel consumption. It should also be noted that the implementation of pressure profiles in the simulation of ignition delay times (IGT) did not noticeably influence the numerical results.

Discussing about the NTC phenomena, occurrence of this behaviour relates with the low temperature equilibrium of $cyC_6H_{11} + O_2 \leftrightarrows cyC_6H_{11}OO$. A shift in the direction of this equilibrium towards the higher production of $cyC_6H_{11}OO$, favours the transition of the overall oxidation chemistry from high temperature to the low temperature kinetics. While the rate of the forward reaction is larger than the backward rate (equilibrium constant, $K_{eq} > 1$) more peroxy radicals are delivered and the low temperature chemistry is more dominant. Throughout a change in the direction of this equilibrium at around T = 800 K, where the backward kinetic of the equilibrium ($cyC_6H_{11}OO \rightarrow cyC_6H_{11} + O_2$) becomes faster than the forward ($cyC_6H_{11} + O_2 \rightarrow cyC_6H_{11}OO$), the higher formation of olefins and a slower ignition at higher temperatures is expected (Fig 5.3).

Fig 5.3a demonstrates schematically the correlation between NTC and the mentioned equilibrium. Fig 5.3b depicts the ratio of the forward to the backward reaction rates of the $cyC_6H_{11}+O_2 \leftrightarrows cyC_6H_{11}OO$ reaction over the temperature range of 300-1500 K. According to the implemented thermochemistry, the cyclohexyl peroxy production dominates the overall investigated temperature interval and thus no shift takes place within low and intermediate temperature ranges. However, it is noticed that, with increase of temperature, the rate of the forward reaction starts to decline, whereas the backward reaction rate increases.

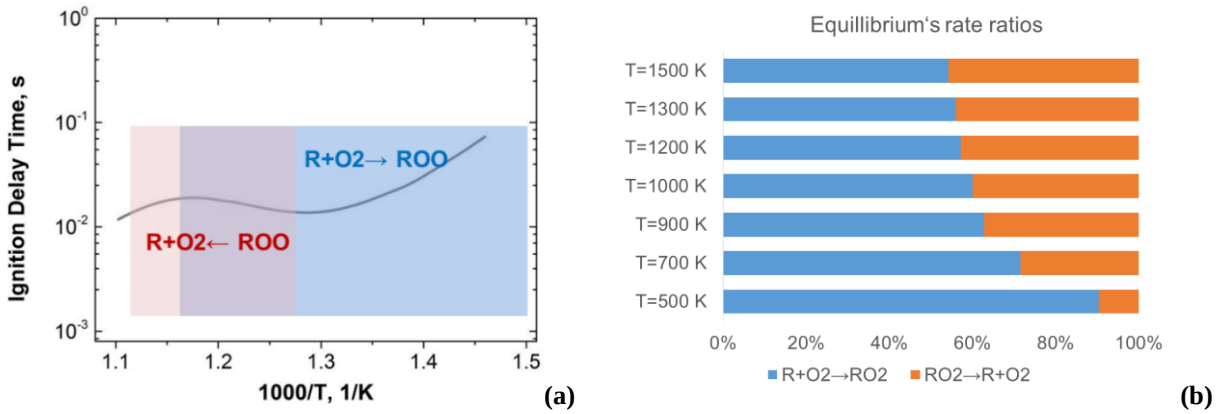


Figure 5.3 Change of the kinetic of $R+O_2 \leftrightarrows ROO$ and appearance on NTC region.

Similar analyses have been carried out for the chain branching and chain propagation reactions. It has been seen that, under the current kinetic data used in the model, the chain branching reactions did not have any sharp shift in equilibriums with the temperature increase [64]. However, a gradual increase of backward reaction rates was observed, which resulted in the smooth transition of dominants from the chain branching steps to the chain propagation reactions.

Both, thermodynamic and the conformational aspects of the cyclohexane structure, i.e., the equilibrium shift to the cyclohexyl peroxy production, and the faster reaction rates for the cycloperoxy isomerization to the cyclohydroperoxy, degrade any pronounced two-stage behaviour in the cyC_6H_{12} ignition. Instead that, the deceleration of ignition delay time growth with temperature decrease, i.e., a Region of Gradient Change (RGC), can be observed as a response to the acceleration of the low temperature reaction rates. The simulations of ignition delay data obtained in shock tubes support this conclusion.

The recent ST experiments performed by Naumann et al. [42], and the ST experiment of Daley et al. [37], Fig 5.4 and Fig 5.5 respectively, do not support the idea of a clear NTC region. Nevertheless, a change in reactivity gradient with temperature decrease, around T < 900 K has been found, which can be seen as an indication for RGC. At higher pressures, the changes in the gradient reactivity are even more pronounced.

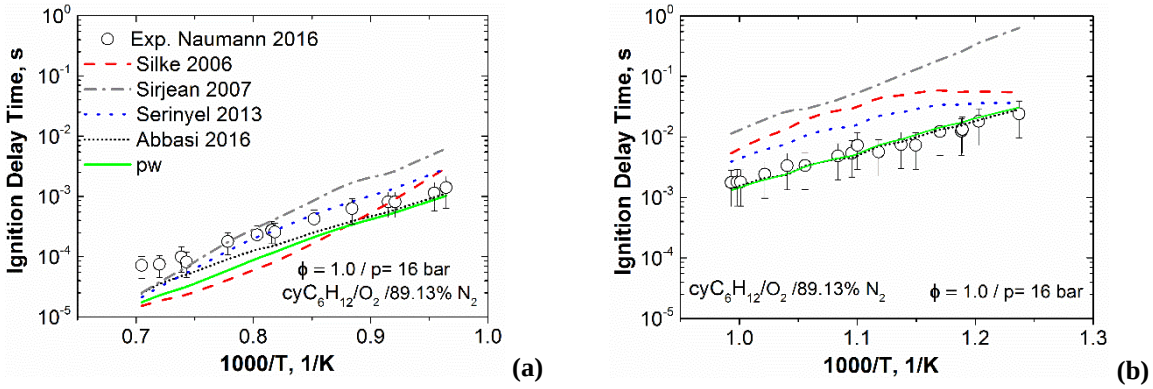


Figure 5.4 Comparison of the ST ignition delay time measurements of Naumann et al. [42] with simulations performed with models [9, 27, 30, 55] and presented work (pw) for [42] for stoichiometric cyclohexane/air mixtures (diluted 1:2 in N_2) at p_5 = 16 bar: a) T_5 = 800-1010 K, b) T_5 = 1030-1420 K. The open symbols and the lines represent the experimental data and the simulations, respectively.

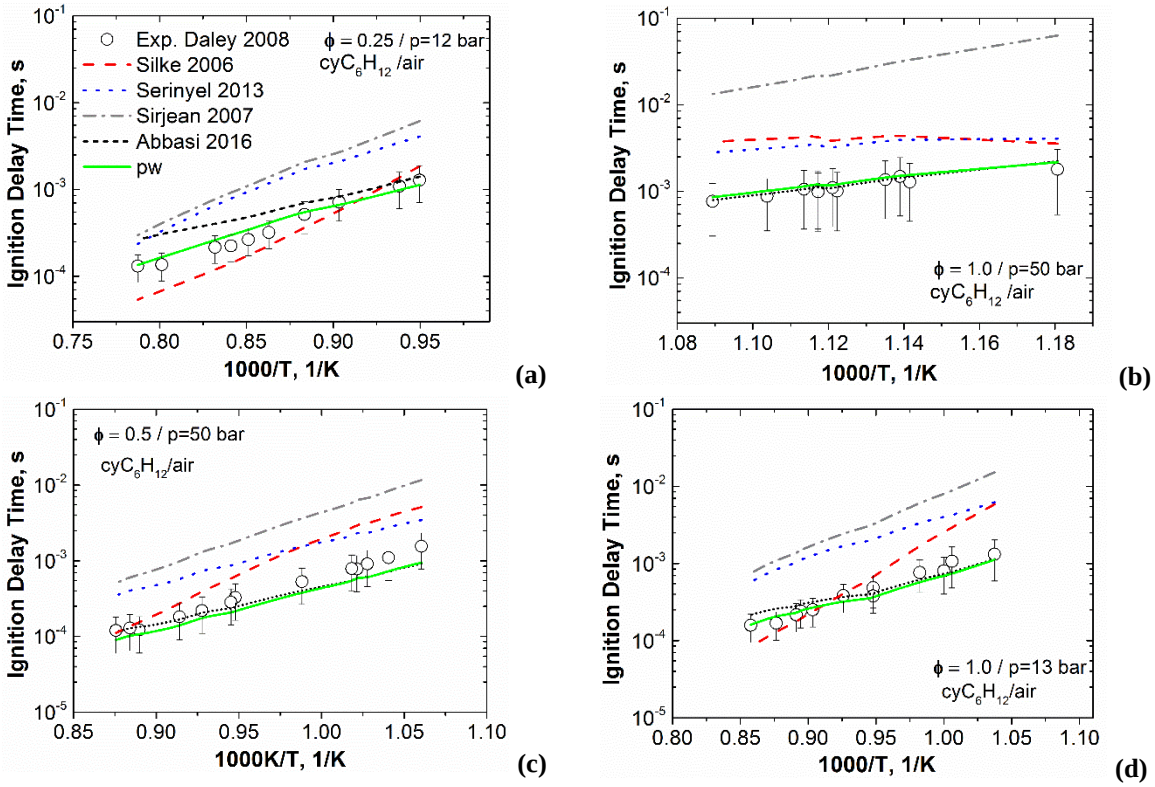


Figure 5.5 Comparison of the ST ignition delay time measurements of Daley et al. [37] with simulations performed with models [9, 27, 30, 55] and presented work (pw) for mixtures of cyclohexane/air at: a) φ = 0.25, p_5 = 12 bar, b) φ = 1.0, p_5 = 50 bar, c) φ = 0.5, p_5 =50 bar, and d) φ = 1.0, p_5 = 13 bar. The open symbols and the lines represent the experimental data and the simulations, respectively.

The models of Silke et al. [9] and Serinyel et al. [30], which showed a good performance on the IGT data from RCM, mostly overpredict these sets of ST data. They failed to generate the trends of experimental data, specifically in low temperatures, Fig 5.4b and Fig 5.5b, d. The lower reactivity in these models could be related to the applied thermochemical properties, but mainly due to the high concentration of olefins, predicted by their models in corresponded temperatures. That is the reason, why results of their models were well-matched with the detected NTC behaviour in RCM experimental data [31, 38], Fig 5.2.

Fig 5.6 shows the OH concentration and temperature profiles, simulated by current model at around 800 K, 824 K, and 854 K based on the experimental conditions of Naumann et al. [42].

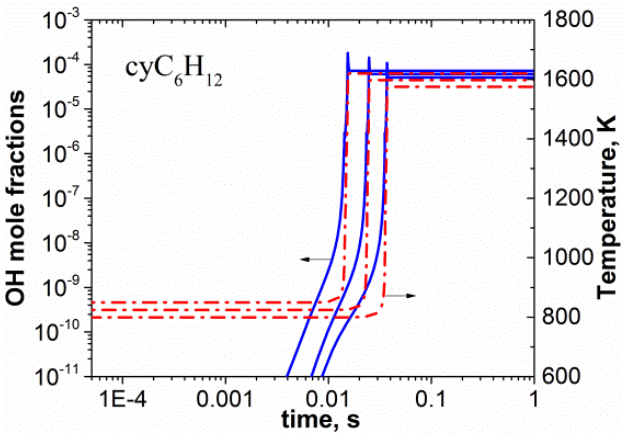


Figure 5.6 Simulation of OH concentration (blue lines) and T profiles (red dash-dot lines) versus time, from experiment of Naumann et al. [42] for stoichiometric cyclohexane/air mixtures (diluted 1:2 in N_2) at T_5 = 800 K, 824 K, 854 K and p_5 = 16 bar.

This can be understood that, at intermediate temperatures, no tendency towards two-stage ignition is predicted by the model. This is also in accordance with the previous explanation about the gradual change in reactivity and existence of RGC.

The gradual increase of reactivity is interpreted throughout three main competitive reaction pathways: the high temperature formation of olefins and products of the β-scission reactions; the chain branching peroxy- and hydroperoxy-radical reactions; and the cyclohexanone and bicyclic ethers (a, b, c, d-cy$C_6H_{10}O$) production. These are observable in species rate of production diagrams in Fig 5.7.

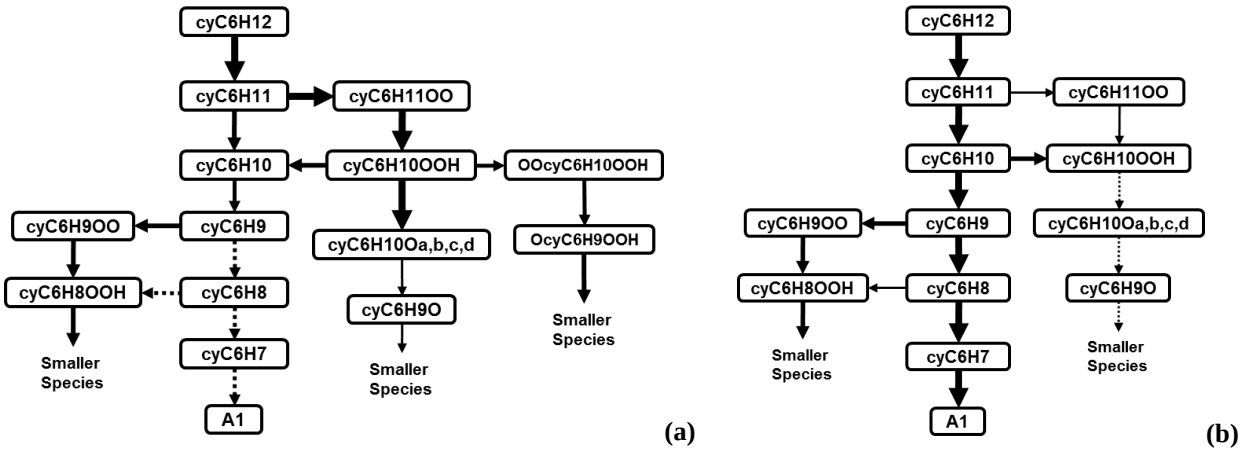


Figure 5.7 Rate of production analysis in p = 16 atm and: a) T = 808 K, b) T = 1389 K. Thickness of arrows is proportional to the rate of paths; the dash-lines represent lower rate of productions than the average threshold.

In the low temperature oxidation regime, after the first O_2 addition and isomerization steps, the cy$OOC_6H_{10}OOH$ formation reaction paths (rooted in reaction *type XII*, see Fig 2.2) competes with a, b, c, d-cy$C_6H_{10}O$ chain-propagation paths (starts with reaction *type XI*, Fig 2.2). The newly added reaction pathway, i.e., cyclohexene low temperature oxidation reactions which initiates whit cyC_6H_9OO formation (*type XX*, Fig 2.2), influences the overall reaction for both temperature regimes, Fig 5.7a, b.

With the temperature increase, the influence of the cy$OOC_6H_{10}OOH$ chain-branching reactions diminishes. However, the cyclohexanone and bicyclic ethers (a, b, c, d-cy$C_6H_{10}O$) production, influences further the overall reactivity, competing with the high-temperature reactions. That proceeds due to the shift in cy$C_6H_{10}OOH \leftrightarrows$ cyC_6H_{10} + HO_2 equilibrium to the left side. This path compensates the decrease of the cyclo-hydroperoxy production through the cyclo-peroxy isomerization, which leads to the chain-propagation of cyclohexanone and bicyclic ethers, and diminishes formation of olefins and HO_2 radicals, Fig 5.7b.

Fig 5.8 provides the simulations of the ignition delay time data from ST experiment of Sirjean [27] in high temperature ranges. The comparisons reveal that, both models of Sirjean et al. [27] and Serinyel et al. [30] deliver better agreements with their experimental data. The current mechanism (present work) also delivers a consistent performance with experimental data, especially in the case of the rich mixture, Fig 5.8a. The overall performance of the new model has been improved compared with the previous version in predicting the trends. However, the data in lean conditions are still overpredicted (Fig 5.8b). The mechanism of Silke et al. [9], which could successfully regenerate the RCM data in low temperature, was not able to describe Sirjean's ST data with desirable accuracy and trend. This has been also observed in other shock tube data, even in low temperature ranges: see Fig 5.4 and Fig 5.5.

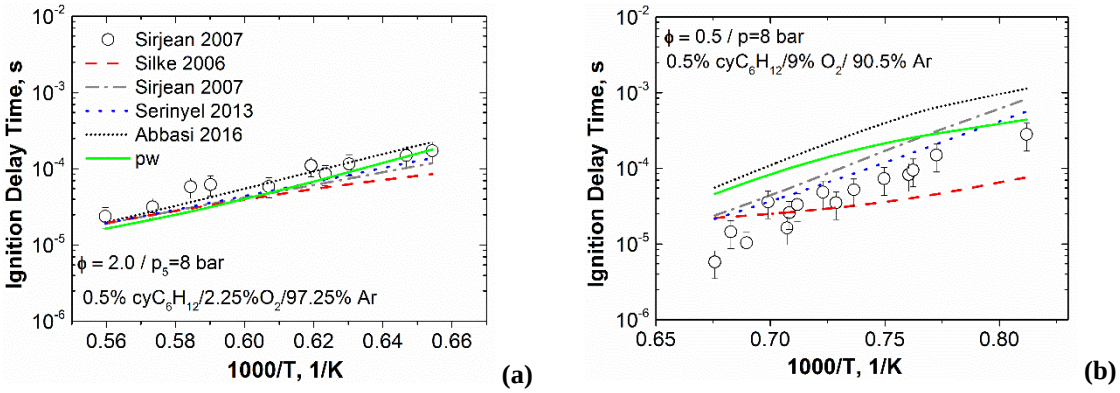


Figure 5.8 Comparison of the ST measurement of Sirjean et al. [27] with simulations performed with several models [9, 27, 30, 55] and presented work (pw) with the for diluted mixtures of cyclohexane/O_2 in Ar at p_5=8 bar: a) T_5=1500-1800 K, φ=2.0, b) T_5=1200-1500 K, φ=0.5. The open symbols and the lines represent the experimental data and the simulations, respectively.

5.2.4. Validation on Flame Speed Experiments

The current mechanism has been also validated on the several sets of experimental flame speed data [30, 32, 35, 36, 41]: see Fig 5.9. The model demonstrates good consistency with experimental data, and reflects the heat release in the system. It is able to describe datasets at atmospheric and elevated pressure, as well as different preheat temperatures with a good agreement. The simulations were also performed with the model Serinyel et al. [30]. At standard temperature and atmospheric pressure, both simulations revealed an excellent accordance with experimental data in lean zone. However, in case of the data of Davis et al. [32], the model of Serinyel et al. [30] overpredicts the rich region φ ≥ 1.15, Fig 5.9a.

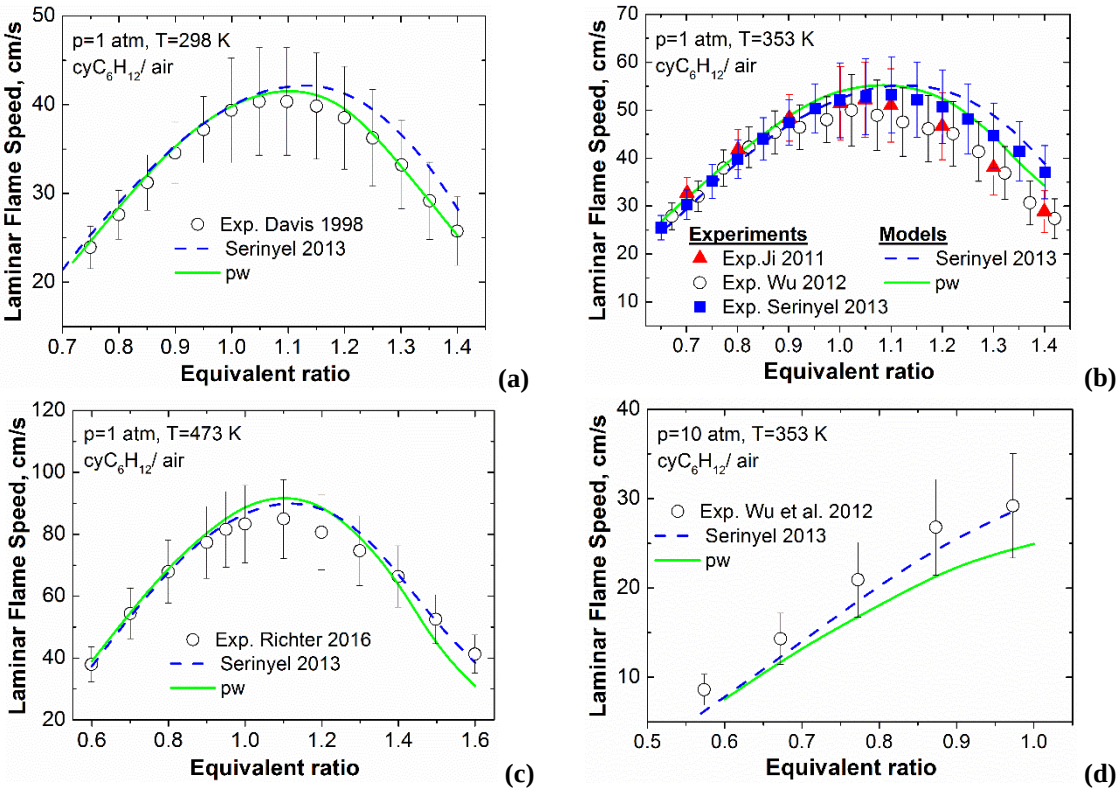


Figure 5.9 Cyclohexane laminar flame speed [30, 32, 35, 36, 41]. The symbols and the lines represent the experimental data and the simulations, respectively. *Note:* pw: present work.

On the Fig 5.9b several flame speed measurements of preheated mixture of cyclohexane and synthetic air at atmospheric pressure were collected. For $\varphi \geq 0.9$ the measured flame speed values by Ji et al. [35] and Wu et al. [36] are about 4-5 $cm \cdot s^{-1}$ lower than experimentally determined by Serinyel et al. [30]. It is seen that, the model of Serinyel et al. [30] predicts the peak position at around φ=1.15, whereas it was observed between φ=1.0-1.1 by all other references. The current model delivers more consistent performance on all three data sets, compared with the model of Serinyel et al [30]. This is specifically clearer to see within the fuel-rich conditions. Fig 5.9c displays the simulation of experimental data of [41] in atmospheric and preheated conditions (T_0=473 K). Both simulations deliver good agreements with experimental data, with a narrow overprediction within the mixture ratio interval of φ=1.01-1.3. For φ>1.4 the model of Serinyel et al. [30] provides better consistence with the observed values, whereas the simulation with current model slightly underpredicts the values, with maximum deviation of 25% at around φ=1.6.

The flame speed data at T_0=353 K and elevated pressure of p=10 atm [36] were also subject of this study, Fig 5.8d. The current mechanism delivers consistent results within the evaluated uncertainty ranges, however with maximum underestimation of 4.5 $cm \cdot s^{-1}$. The mechanism of Serinyel et al. [30] shows very good agreement with experimental data.

5.2.5. The Model Validation on the Data from Burner-Stabilized Flames

5.2.5.1. Concentration Profiles of Species Important for Soot Formation

The formation of soot particles is known to be mainly influenced by growth and conglomeration of PAH molecules in fuel rich flames [135]. Since the combustion of cyclic fuels, compared with the linear ones, can potentially increase the level of formation of aromatic molecules, studying of reaction paths leading to PAH and their precursors in cyclohexane flame is also in our focus. This is particularly important, since the well-established cyclohexane models, were not aimed at investigating this matter. They do not even include any detailed PAH kinetics and that is why, the burner-stabilized flames data have been rarely used by them as validation mean.

For this aim the current mechanism has been analysed and validated on two different sets of data of burner-stabilized flames: the stoichiometric mixture of cyclohexane and oxygen, stabilized in 32.5% Ar at low pressure of p = 30 Torr, and initial temperature of 1000 K studied by Law et al. [34]; and the preheat (T_0 = 700 K) fuel-rich (φ = 2.33) flame of cyclohexane and O_2, diluted in 39.4% N_2 investigated by Ciajolo et al. [40] at atmospheric pressure. Fig 5.10 and Fig 5.11 show simulations of these stabilized flames, respectively.

In the case of first dataset, the concentration profiles of main combustion products, i.e., H_2, H_2O, and CO_2 were in good agreement with experimental values (Fig 5.10a,b,c). The concentration profiles of C_3H_6, and C_3H_3 were reproduced successfully (Fig 5.10e,f). The concentration profile of C_3H_4 was slightly overpredicted (Fig 5.10d) and the C_2H_2 concentration was determined smaller than the experimental values (Fig 5.10e). Also, the simulated profiles of initial cyclic and aromatic precursors, namely cyC_5H_5 and benzene (C_6H_6, A1), were consistent with the experimental data, although the A1 concentration was below the measurements by a factor of 7 (Fig 5.10g,h).

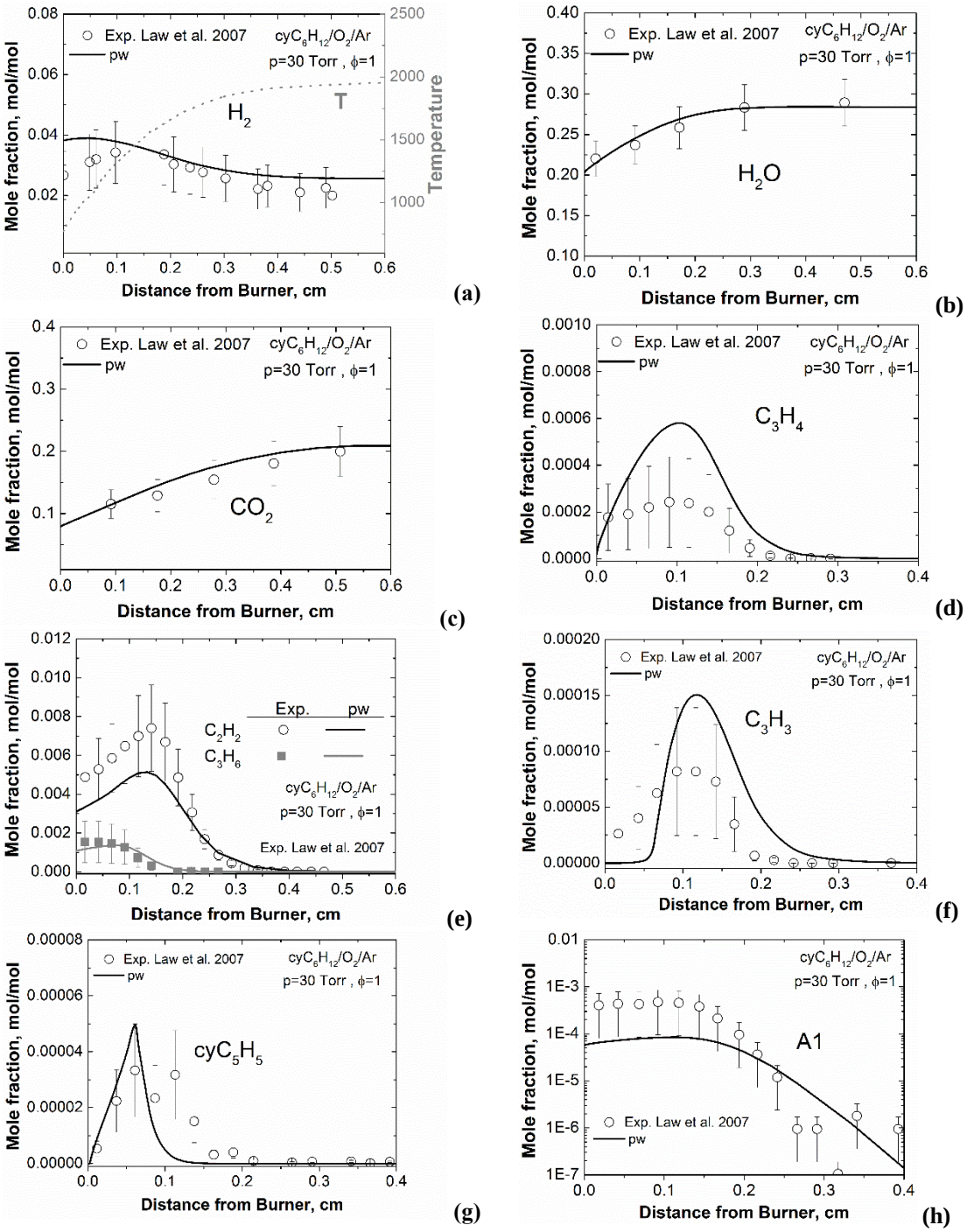


Figure 5.10 Species concentration profiles measured in the burn-stabilized flame of Law et al. [34]. Solid lines represent the current simulations; data uncertainties were evaluated as 20% for major combustion species and 30-50% for other intermediates.

The simulation results of the fuel-rich flame of Ciajolo et al. [40], presented in Fig 5.11, similarly demonstrated that the developed model successfully reproduced the measured concentration profiles for the main combustion products and PAH precursors, within the desired uncertainty intervals. Unlike the simulations of data Law et al. [34], The concentration of A1 was slightly overpredicted (Fig 5.11f). The difference in prediction behaviour of benzene profile might be due to the experimental uncertainties between Law et al. [34] and Ciajolo et al. [40], but also proves the existing inconsistency between them. However, it has to be noticed that the data of Ciajolo et al. [40] was extracted from richer flame, which supposed to produce higher content of aromatics than the stoichiometric flame of Law et al. [34].

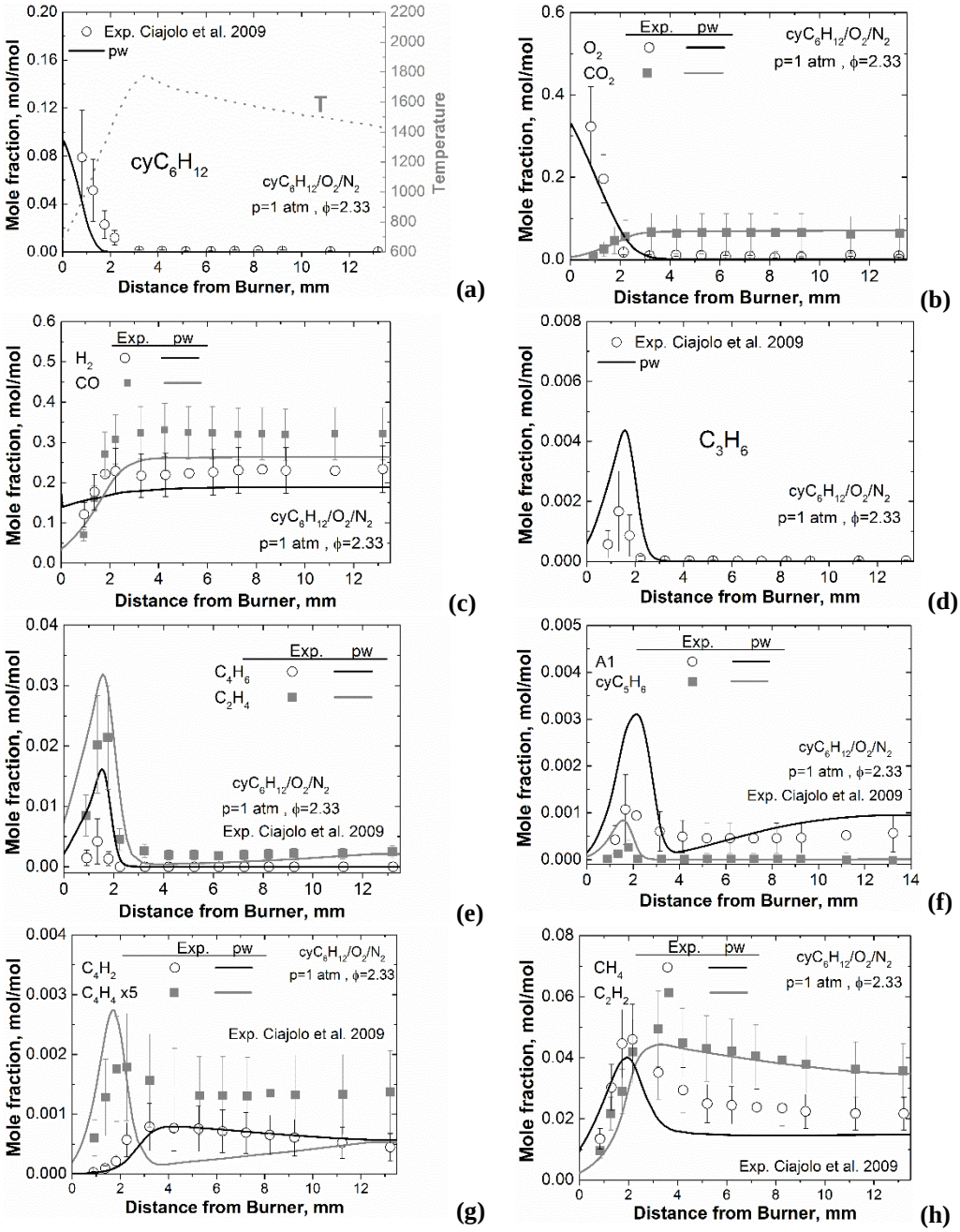


Figure 5.11 Species concentration profiles measured in the burn-stabilized flame of Ciajolo et al. [40].The solid lines represent the current simulations; data uncertainties were evaluated as 20% for major combustion species and 30-50% for other intermediates.

5.2.5.2. Routs for Benzene Productions in High and Low Temperature Regimes

The sensitivity and rate of production analysis have been carried out at three different temperature zones along the given temperature profiles of Ciajolo et al. [40] measurement:
a) within the area with T < 1600 K, Fig 5.12; b) within the active reaction zone (occurring shortly after the maximum temperature) Fig 5.13, and c) in the post flame area at a certain distance far above the burner, Fig 5.14. The pathways from the fuel until the formation of the substituted mono-aromatics, such as Benzene (C_6H_6, A1) and Toluene (C_7H_8), as well as the large PAH, such as pyrene ($C_{16}H_{10}$, A4), chrysene ($C_{18}H_{12}$) and benzo-pyrene ($C_{20}H_{12}$, BAPYR) have been studied. It is shown that, for T < 1600 K, the cascading dehydrogenation is the main reacting path toward the benzene (A1) formation. The secondary ways within this zone towards the formation

of mono-aromatics, as well as larger aromatics such as indene (C_9H_8), are the recombination of allene (C_3H_4), propargyl radical (C_3H_3, H_2CCCH), and acetylene (C_2H_2). Under the investigated temperature regime (T < 1600 K), these pathways are initiated after direct dissociation and fuel dehydrogenation processes.

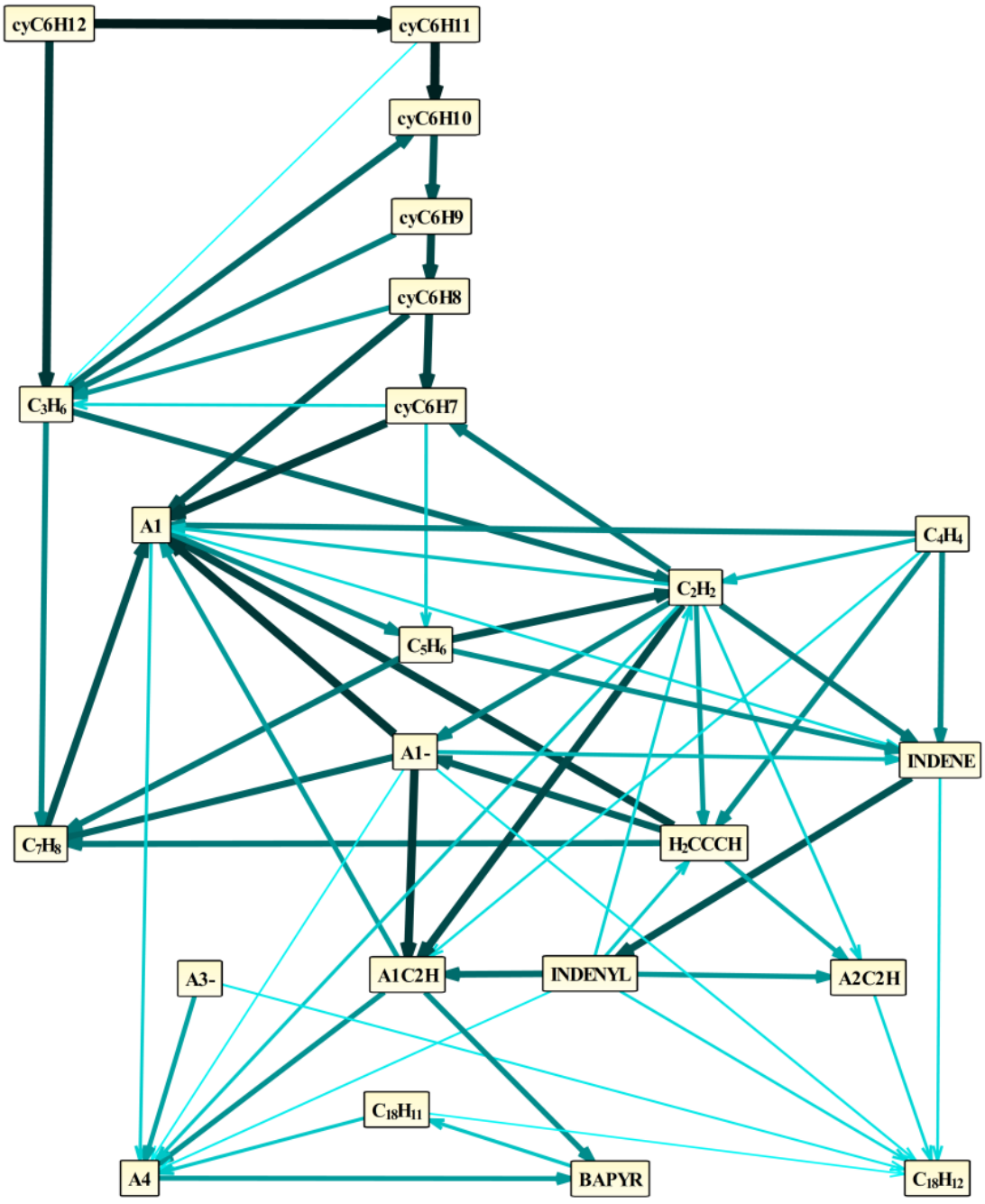


Figure 5.12 Species rate of production analysis performed with Chemical Work Bench (CWB) software package [136] at p = 1atm, T = 1380 K and 1.9 mm above the burner, where also maximum amount of benzene (A1) was reported. Thickness and darkness of the arrows is proportional to rate of the pathways; higher rates are specified by thick-dark arrows and lower rates are presented by bright-narrow arrows.
Note: A1: Benzene (C_6H_6), A1-: Phenyl (C_6H_5), A1C$_2$H: Phenyl acetylene ($C_6H_5C_2H_3$), INDENE: Indene (C_9H_8), INDENYL: Indenyl radical (C_9H_7), A2: Naphthalene ($C_{10}H_8$), A2C$_2$H: Ethynylnaphthalene ($C_{12}H_8$), A3: Phenanthrene ($C_{14}H_{10}$), A3-: Phenanthryl radical ($C_{14}H_9$), A4: Pyrene ($C_{16}H_{10}$), BAPYR: Benzo(a)py-rene ($C_{20}H_{12}$).

At T > 1600 K, that occurs at the end of the main reaction zone, the recombination of smaller PAH precursors (C_2-C_4 chemistries), the propargyl radical (C_3H_3), C_2H_2 and C_4H_4, controls the process of benzene formation, Fig 5.13. At this position the fuel is mostly consumed, and PAH continue to conglomerate into larger polyaromatic molecules, such as A4, $C_{20}H_{12}$ and $C_{18}H_{12}$.

Approaching the end of the combustion chamber, the temperature gradually starts to decrease. Fig 5.14 represents the species rate of production analysis at T = 1470 K and the height of Z=11 mm, where the smaller chemistries, collide with each other to form large PAH molecules. The highest concentration of $C_{20}H_{12}$ (BAPYR), $C_{18}H_{12}$, $C_{18}H_{10}$ (A4) and $C_{18}H_{10}$ (BGHIF) are also predicted by the model to be at the top of the burner i.e., at Z = 14 mm, T = 1450 K. This explains the high concentration of soot particles often observed in higher distances from the burner.

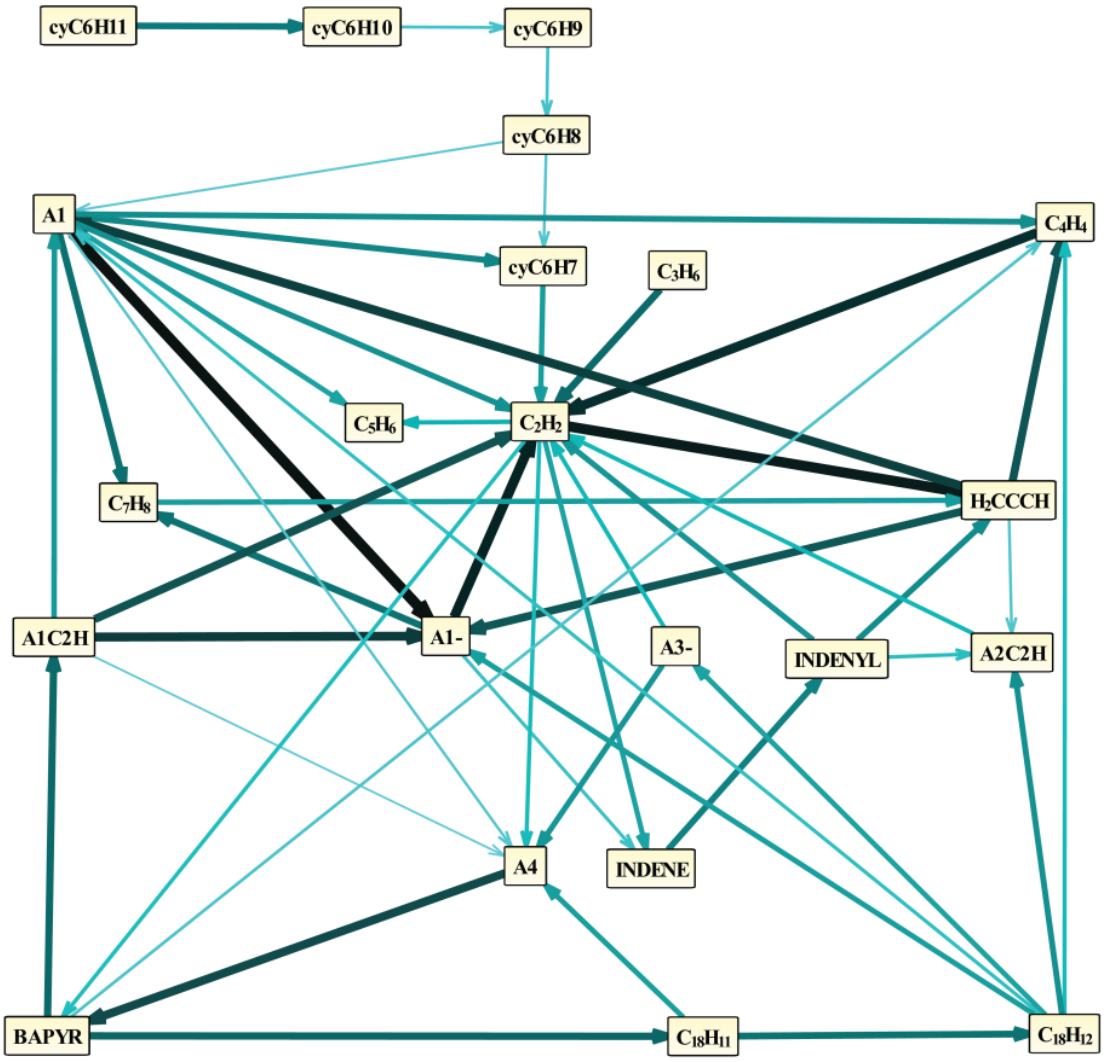


Figure 5.13 Species rate of production analysis performed with Chemical Work Bench (CWB) software package [136] at p = 1atm, T_{max} = 1750 K and 3.8 mm above the burner. Higher production rates are specified by thick-dark arrows and lower rates are presented by bright-narrow arrows.
Note: A1: Benzene (C_6H_6), A1-: Phenyl (C_6H_5), A1C_2H: Phenyl acetylene ($C_6H_5C_2H_3$), INDENE: Indene (C_9H_8), INDENYL: Indenyl radical (C_9H_7), A2: Naphthalene ($C_{10}H_8$), A2C_2H: Ethynylnaphthalene ($C_{12}H_8$), A3: Phenanthrene ($C_{14}H_{10}$), A3-: Phenanthryl radical ($C_{14}H_9$), A4: Pyrene ($C_{16}H_{10}$), BAPYR: Benzo(a)pyrene ($C_{20}H_{12}$).

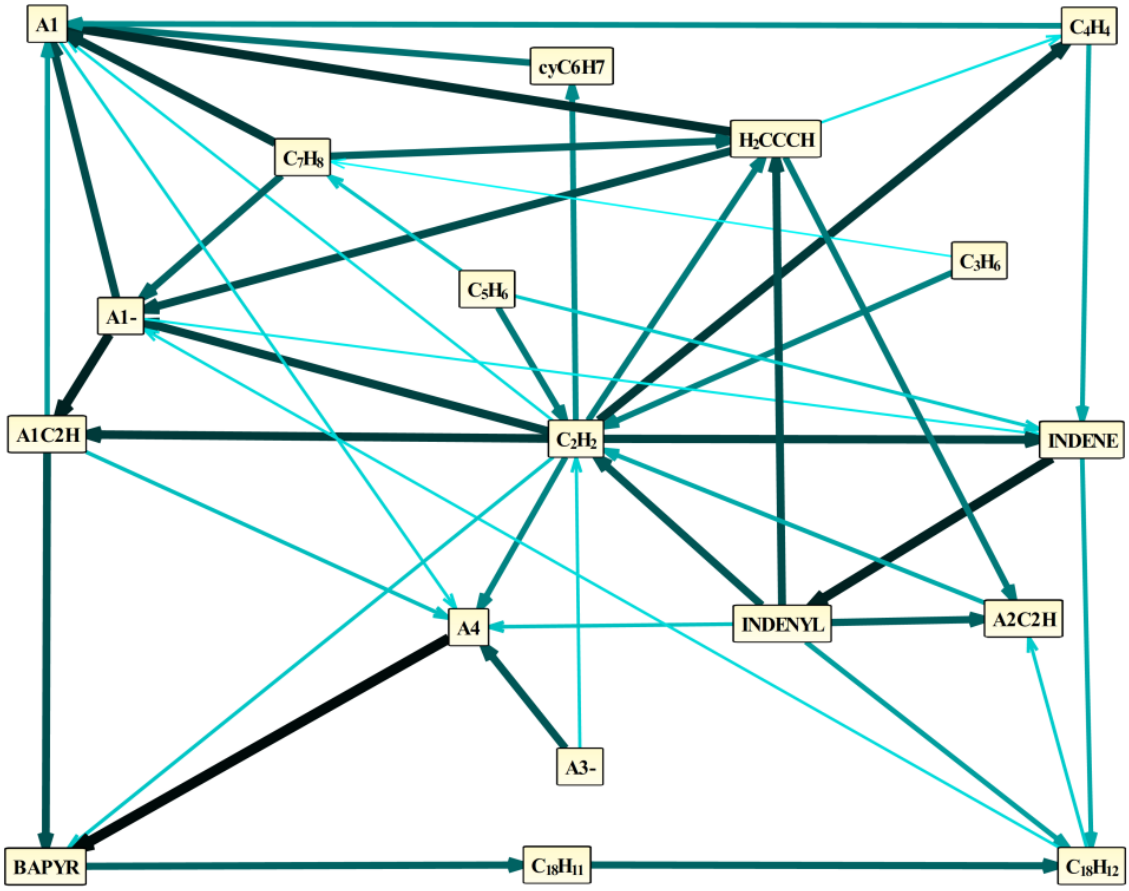


Figure 5.14 Species rate of production analysis performed with Chemical Work Bench (CWB) software package [136] at 11.0 mm above the burner, p = 1atm, T = 1473 K. Higher production rates are specified by thick-dark arrows and lower rates are presented by bright-narrow arrows.
Note: A1: Benzene (C_6H_6), A1-: Phenyl (C_6H_5), A1C$_2$H: Phenyl acetylene ($C_6H_5C_2H_3$), INDENE: Indene (C_9H_8), INDENYL: Indenyl radical (C_9H_7), A2: Naphthalene ($C_{10}H_8$), A2C$_2$H: Ethynylnaphthalene ($C_{12}H_8$), A3: Phenanthrene ($C_{14}H_{10}$), A3-: Phenanthryl radical ($C_{14}H_9$), A4: Pyrene ($C_{16}H_{10}$), BAPYR: Benzo(a)pyrene ($C_{20}H_{12}$).

The schematics of Fig 5.15 graphically simplify these two different formation pathways of the substituted mono-aromatics. It can be pointed out, that for T < 1600 K, the cascading dehydrogenation is the major reaction path towards these aromatics, Fig 5.15a. Within the secondary pathways, the propargyl radical recombination controls the formation process of aromatics (Fig 5.15b). This takes place at T > 1600 K, when cyclohexane is already fully decomposed into allene and acetylene

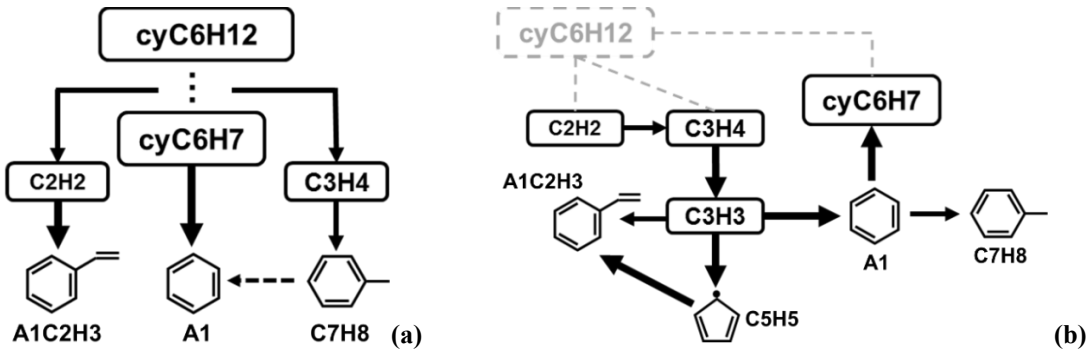


Figure 5.15 Schematics of reaction path analysis results, performed for studied flames at: a) Flame temperature T < 1600 K, and b) T > 1600 K. The grey dash lines on the graphic (b) shows that in this stage the fuel is fully consumed. *Note:* A1: Benzene (C_6H_6), A1C$_2$H$_3$: Styrene ($C_6H_5C_2H_3$).

Conclusions and Future Perspectives

A semi-detailed reaction mechanism for the low and high temperature cyclohexane oxidation with PAH formation was developed. This mechanism is the most recent improved version of previous models of Abbasi et al. [54, 55] where a kinetic model for cyclohexane was obtained through development of cascading dehydrogenation steps, and initial build-up of low temperature chemistry [54]. This work was later updated [55], through further extension of low temperature reaction paths and evaluation of the related kinetic data, revision and estimation of the thermodynamic and transport properties of intermediates, and further validation on the most recent experimental data. In present mechanism certain number of reaction paths were revised and optimized as the result of uncertainty and sensitivity analyses. This mechanism also implements the new optimized syngas and acetylene sub-models for C_0-C_3 chemistry [17-19].

For species important to the cyclohexane sub-model, the required thermodynamic data were estimated using an algorithm with persuasive accuracy and based on Benson group additivity method. Since the available databases for the Benson groups, provided by different references, did not cover all required groups for the purpose of this work, new groups had to be determined. This was done either empirically, using a combinative approach via properties of reference species which contain these new groups (see Table 3.2), or semi-empirically, if there were no known data for the parent molecule with analogous structure in the literature, for instance for the group [C-(C_d)(CO)($H)_2$]. In this case, calculations of bond energy and statistical mechanics analysis have been performed (see Tables 3.3-3.4). The estimated properties of the new groups were compared with literature data (see Table 3.6). For cyclic molecules, including oxygenated and bicyclic species, ring correction groups within T=300-1500 K have been estimated (see Table 3.5).

Additionally, for a selected number of species, thermodynamic properties have been estimated and compared with available data from different sources (see Tables 3.7-3.8). The evaluated properties for relevant species in cyclohexane combustion were also provided and compared with similar ones in various kinetic databases (see Fig 3.2 and Table 3.9). The FORTRAN code "THERM-PLY" was further developed in this work to estimate these properties in the form of NASA polynomial coefficients within T=300-1500 K, and then to extrapolate them up to temperature of 3500 K (see Appendices II,V).

Main transport properties have been either empirically or analogously determined. The Lennard-Jones parameters were fixed via determination of boiling and critical temperature and pressure of the species. The additivity method of Joback and Reid [99] was employed to approximate the boiling temperature, critical temperature and critical pressure via structural group contributions. The polarizability was also calculated by the additive empirical method proposed by Bosque et al. [122]. The dipole moments and rotational relaxation number for new species were evaluated analogous to other known molecules, regarding geometrical parameters, size of the molecules and their chemical functional groups (see Table 4.2).

The development of the kinetic model was based on data consistency and uncertainty analysis among the available literature data. The modifications were focused on cyclohexane sub-mechanism. Special attention was paid to the low temperature chemistry and second stage oxidation of cyclohexene (see Fig 2.2), and revision of reaction rate for certain reactions. The

reactions were selected based on the outcome of sensitivity analysis, performed at several targets (Fig 5.1), and the available results of reaction rate uncertainty analysis for selected reaction paths (Table 2.2, Fig 2.6, Table 5.2). The uncertainty analysis was carried out using the "REAC-UQ" tool [19], which implements the FUMILI optimization scheme [69, 70, 71], in order to estimate the mean reaction rate coefficients, and to quantify the uncertainty intervals. This analysis has shown high degree of uncertainty among the kinetic data for several key reactions, reported by several cyclohexane oxidation studies (see Fig 2.6 and Table 2.2).

The reaction model was successfully validated on various types of experimental data: ignition delay times measured in Rapid Compression Machine (RCM) and Shock-Tube (ST) experiments (Fig 5.2, Fig 5.4, Fig 5.5, Fig 5.8), laminar flame speed data (Fig 5.9), and species mole fraction profiles (Fig 5.10, Fig 5.11). The performance of the new model has been compared with results from previous mechanisms, as well as with other well-known cyclohexane models. In the case of RCM experiments, in spite of the mentioned modifications, any strong Negative Temperature Coefficient (NTC), as described in RCMs and also predicted by the models of Silke et al. [9] and Serinyel et al. [30] between 700-900 K, was not predicted by current model. However, it must be noted that no NTC effect was detected by other different ST experiments in low and intermediate temperature ranges. Instead of NTC behaviour, the Region of Gradient Change (RGC) was observed. The RGC emerged as the result of an increase in reactivity by temperature decrease, and as a gradual buffer zone of transition from high temperature oxidation to low temperature. This can be interpreted as a response to the competition between low and high temperature reaction schemes. This was also well-predicted and produced by current model.

The kinetic mechanism successfully describes the available flame speed data with high precision. It has also been compared with the results of the well-established mechanism of Serinyel et al. [30]. In most cases, the new mechanism delivered even more precise results in comparison with mechanism of Serinyel et al. [30], except at elevated pressure, where our mechanism showed up to 10% deviation from experimental values.

Among the up-to-now published studies of cyclohexane combustion, this is the first time that the formation of PAH paths at different positions and temperature regimes of cyclohexane are extensively investigated. The current mechanism was able to successfully describe the concentration profiles of important PAH precursors from different burn stabilized flame data. It has been concluded that at $T < 1600$ K, the cascading dehydrogenation is the main controlling pathway of benzene formation, rather than the formation via small precursors, such as propargyl radical (C_3H_3). At $T > 1600$ K, where the fuel is completely consumed, recombination of smaller PAH precursors, mainly propargyl, acetylene (C_2H_2) and 1-Buten-3-yne (C_4H_4) are more influential (see Fig 5.12, Fig 5.13 and Fig 5.15). It has also been found that under the mentioned temperature regime, the mono-aromatics are formed and conglomerate into larger poly-aromatic molecules, such as pyrene ($C_{16}H_{10}$, A_4), benzo[a]pyren ($C_{20}H_{12}$, BAPYR) and chrysene ($C_{18}H_{12}$), Fig 5.14.

As future research perspectives, further development of kinetic mechanism on larger and more complex cyclic naphthenes, would be one of our main research goals. This can be achieved through development of n-propylcyclohexane sub-model, based on the current scheme of cyclohexane oxidation. It would be specifically interesting to investigate possible differences between cyclohexane and n-propylcyclohexane oxidation, especially regarding the existence of NTC region, and PAH formation pathways.

References

[1] The Economist, "$20 is the new $40, Why the oil price has plunged," 16 1 2016. [Online]. Available: https://www.economist.com/news/finance-and-economics/21688446-why-oil-price-has-plunged-20-new-40. [Accessed 28.05.2019].

[2] Saibov, A. "In-Depth Characterization of Synthetic GTL Jet Fuel Combustion Performance," Stuttgart: Chemical Kinetics Department, Universität Stuttgart, 2012.

[3] Zizin, A. "Development of a Reduced Chemical-Kinetic Combustion Model for Practical Fuels", Stuttgart, Germany: Ph.D. thesis, Faculty of Aerospace Engineering, Universität Stuttgart, Institute of Combustion Technology for Aerospace Engineering, 2013.

[4] Gueret, C., Cathonnet, M., Boettner, J.-C., Gaillard, F., "Experimental Study of Kerosene oxidation in a jet flow reactor," 23th Symposium (International) on Combustion, Combustion Institute, pp. 211-216, 1990.

[5] Faith, L.E., Ackerman, G.H., Henderson, H.T., "Heat sink capability of Jet A fuel: heat transfer and coking studies," NASA CR-72951, July 1971.

[6] Wacker, M., "Auslegungswerkzeuge für Fluggasturbinen mit nachwachsenden Treibstoffen," Stuttgart, Germany: Master thesis, Institute of Combustion Technology of Aerospace Faculty, Universität Stuttgart, 2008.

[7] Slavinskaya, N.A., Zizin, A., "On surrogate fuel formulation," Proc. of GT2009, ASME Turbo Expo 2009: Power for Land, Sea and Air, 2009, Orlando, USA, GT 2009-60012, 2009.

[8] Slavinskaya, N., Zizin, A., Riedel, U., "Towards Kerosene Reaction Model Development: Propylcyclohexane, cyC_9H_{18}, n-Dodecane, $C_{12}H_{26}$, and Hexadecane $C_{16}H_{34}$ Combustion," in 48th AIAA ASM, Orlando, Florida, 2010.

[9] Silke, E. J., Pitz, W. J., Westbrook, C. K., Ribaucour, M., "Detailed Chemical Kinetic Modeling of Cyclohexane Oxidation," J. Phys. Chem. A, vol. 111, 2007, pp. 3761-3775.

[10] Westbrook, C.K., Warnatz, J., Pitz, W.J., "Comparison of Lumped and Molecular Modeling of Hydropyrolysis," 22nd Symposium (International) on Combustion, pp. 893-901, Pittsburgh, 1988.

[11] Chevalier, C., Pitz, W.J., Warnatz, J., Westbrook, C.K., Melenk, H., "Hydrocarbon ignition: Automatic generation of reaction mechanisms and applications to modeling of engine knock," 24th Symposium (International) on Combustion, Pittsburgh, pp. 93-101, 1992.

[12] Westbrook, C.K., Pitz, W.J., Leppard, W.R., "The Autoignition Chemistry of Paraffinic Fuels and Pro-Knock and Anti-Knock Additives: A Detailed Chemical Kinetic Study," in Society of Automotive Engineers publication SAE-912314, 1991.

[13] Ranzi, E., Faravelli, T., Gaffuri,P., Sogaro, A., "A Wide-Range Modeling Study of Iso-Octane Oxidation," Combustion and Flame, vol. 108, pp. 24-42, 1997.

[14] Curran, H.J., Gaffuri, P., Pitz, W.J., Westbrock, C.K., "A Comprehensive Modeling Study of n-Heptane Oxidation," Combustion and Flame, vol. 114, pp. 149-177, 1998.

[15] Curran, H.J., Gaffuri, P., Pitz, W.J., Westbrock, C.K., "A Comprehensive Modeling Study of Iso-Octane Oxidation," Combustion and Flame, vol. 129, pp. 253-280, 2002.

[16] Battin-Leclerc, F., "Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates," Progress in Energy and Combustion Science, vol. 34 pp. 440-498, 2008.

[17] Slavinskaya, N. A., Abbasi, M., Starcke, J. H., Whitside, R., Mirzayeva, A., Riedel, U., Li, W., Oreluk, J., Hegde, A., Packard, A., Frenklach, M., Gerasimov, G., Shatalov, O., "Development of an UQ-Predictive Chemical Reaction Model for Syngas Combustion," Energy and Fuels, vol.31, pp. 2274-2297, 2017.

[18] Slavinskaya, N. A., Abbasi, M., Starcke, J. H., Haidn, O.J., "Methane Skeletal Mechanism for Space Propulsion Applications," 52nd AIAA/SAE/ASEE Joint Propulsion Conference, AIAA Propulsion and Energy Forum, (AIAA 2016-4781) , Salt Lake City, USA, 2016.

[19] Slavinskaya, N. A., Chernov, V., Whitside R., Starke J. H., Mirzayeva, A., Abbasi, M., Auyelkhankyzy, M., "A Modeling Study of Acetylene Oxidation and Pyrolysis," Combustion and Flame, vol. 210, pp. 25-42, 2019.

[20] Braun-Unkhoff, M., Kathrotia, T., Richter, S., Naumann, C., Slavinskaya, N.A., Methling, T., Riedel, U., "Reaction Model Development for Synthetic Jet Fuels: Surrogate Fuels As a Flexible Tool to Predict Their Performance," ASME Turbo Expo 2018: Power for Land, Sea and Air, 10.1115/GT2018-76997l.

[21] Warnatz, J., Maas, U., Dibble, R. W., Combustion (Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation) 4th edition, Heidelberg, Germany: Springer, 2006.

[22] Voisin, D., Marchal, A., Reuillon, M., Boettner, J. C., Cathonnet, M., "Experimental and Kinetic Modeling Study of Cyclohexane Oxidation in a JSR at High Pressure," Combustion Science and Technology, vol. 138, pp. 137-158, 1998.

[23] El Bakali, A., Braun-Unkhoff, M., Dagaut, P., Frank, P., Cathonnet, M., "Detailed Kinetic Reaction Mechanism for Cyclohexane Oxidation at Pressure up to Ten Atmospheres," Proceedings of the Combustion Institute, vol. 28, pp. 1631-1638, 2000.

[24] Ristori, A., Dagaut, P., El Bakali, A., Cathonnet, M., "The Oxidation of N-Propylcyclohexane: Experimental Results and Kinetic Modeling," Combustion Science and Technology, vol. 165, pp. 197-228, 2001.

[25] Granata, S., Faravelli, T., Ranzi, E., "A wide range kinetic modeling study of the pyrolysis and combustion of naphthenes," Combustion and Flame, vol. 132, pp. 533-544, 2003.

[26] Zhang, H. R., Huynh, L.K., Kungwan, N., Yang, Z., Zhang, S., "Combustion Modeling and Kinetic Rate Calculations for a Stoichiometric Cyclohexane Flame.1. Major Reaction Pathways," J. Phys. Chem. A, Vol. 111, pp. 4102-4115, 2007.

[27] Sirjean, B., Buda, F., Hakka, H., Glaude, P.A., Fournet, R., Warth, V., Battin-Leclerc, F., Lopez, M. R., "The Autoignition of Cyclopentane and Cyclohexane in a Shock Tube," Proceedings of the Combustion Institute, vol. 31, pp. 277-284, 2007.

[28] Cavallotti, C., Rota, R., Faravelli, T., Ranzi, E., "Ab initio evaluation of primary cyclo-hexane oxidation reaction rates," Proceedings of the Combustion Institute, vol. 31, pp. 201-209, 2007.

[29] Buda, F., Heyberger, B., Fournet, R., Glaude, P.A., Warth, V., Battin-Leclerc, F., "Modeling of the Gas-Phase Oxidation of Cyclohexane," Energy & Fuels, vol. 20, 1450-1459, 2006.

[30] Serinyel, Z., Herbinet, O., Frottier, O., Dirrenberger, P., Warth, V., Glaude, P.A., Battin-Leclerc, F., "An experimental and modeling study of the low- and high-temperature oxidation of cyclohexane," Combustion and Flame, vol. 160, pp. 2319-2332, 2013.

[31] Lemaire, O., Ribaucour, M., Carlier, M., Minetti, R., "The Production of Benzene in the Low-Temperature Oxidation of Cyclohexane, Cyclohexene, and Cyclohexa-1,3-diene," Combust and Flame,vol. 127, pp. 1971-1980, 2001.

[32] Davis, S. G., Law, C. K., "Determination of and Fuel Structure Effects on Laminar Flame Speeds of C1 to C8 Hydrocarbons," Combustion Science and Technology, vol. 140, pp. 427-449, 1998.

[33] Law, M. E., "Molecular-beam mass spectrometry of ethylene and cyclohexane flame," Ph. D. Dissertation, Department of Chemical Engineering, University of Massachusetts Amherst, 2005.

[34] Law, M. E., Westmoreland, P. R., Cool, T. A., Wang, J., Hansen, N., Kasper, T., "Benzene precursors and Formation Routes in a Stoichiometric Cyclohexane Flame," Proceedings of the Combustion Institute, vol. 31, pp.565-573, 2007.

[35] Ji, C., Dames, E., Sirjean, B., Wang, H., Egolfopoulos, F.N., "An experimental and modeling study of the propagation of cyclohexane and mono-alkylated cyclohexane flames," Proceedings of the Combustion Institute, vol. 33, pp. 971-978, 2011.

[36] Wu, F., Kelley, A.P., Law, C.K., "Laminar flame speeds of cyclohexane and mono-alkylated cyclohexanes at elevated pressures," Combust and Flame, vol. 159, pp. 1417-1425, 2012.

[37] Daley, S. M., Berkowitz, A.M., Oehlschlaeger, M.A., "A Shock Tube Study of Cyclopentane and Cyclohexane Ignition at Elevated Pressures," International Journal of Chemical Kinetics, vol. 40, nr. 10, pp. 624-634, 2008.

[38] Vranckx, S., Lee, C., Chakravarty, H.K., Fernandes, R.X., "A rapid Compression Machine Study of the Low Temperature Combustion of Cyclohexane at Elevated Pressures," Proceedings of the Combustion Institute, vol. 34, pp. 377-384, 2012.

[39] Hong, Z., Lam, K.-Y., Davidson, D.F., Hanson, R.K., Combust. Flame 158 (2011) 1456–1468.

[40] Ciajolo, A., Tergrossi, A., Mallardo, M., Faravelli, T., Ranzi, E., "Experimental and Kinetic Modeling Study of Sooting Atmospheric-Pressure Cyclohexane Flame," Proceedings of the Combustion Institute, vol. 32, pp. 585-591, 2009.

[41] Richter, S., Raida, M. B., Naumann, C., Riedel, U., "Measurement of the Laminar Burning Velocity of Neat Jet Fuel Components," Proceedings of the World Congress on Momentum, Heat and Mass Transfer (MHMT'16), Paper nr. CSP 115, Prague-Czech Republic, April 2016.

[42] Naumann, C. et al., "InnoTreib - Innovative Treibstoffe der Zukunft," Bundesministerium für Wirtschaft und Energie (BMWi), Interim reports AP 4.2 and AP 6 from 05.08.2016, Rept. FKZ 20E1310, 2016.

[43] Richter, S., Naumann, C., Riedel, U., "Experimental study on the combustion properties of an Alcohol-to-Jet fuel," in Proceedings of the 2nd World Congress on Momentum, Heat and Mass Transfer (MHMT'17), Paper nr. CSP 107, Barcelona, Spain , April 7– 8, 2017.

[44] Zeppieri, S., Brezinsky, K., Glassman, I., "Pyrolysis studies of methylcyclohexane and oxidation studies of methylcyclohexane and methylcyclohexane/toluene blends," Combustion and Flame, vol. 108, pp. 266-286, 1997.

[45] Tsang, W., "Thermal Stability of Alcohols," Int. J. Chem. Kinetics, vol. 8, pp. 173–192, 1976.

[46] Zeelenberg, A. P., Bruijn H. W., "Kinetics, Mechanism and Products of the Gaseous Oxidation of Cyclohexane," Combust and Flame, vol. 9, pp. 281-295, 1965.

[47] Klaï, S. E., Baronnet, F., "Etude de l'oxydation homogene du cyclohexane en phase Gazeuse," J. Chim. Phys., vol. 90, pp. 1951-1998, 1993.

[48] Sirjean, B., Glaude, P. A., Ruiz-Lopèz, M. F., Fournet, R., "Theoretical Kinetic Study of Thermal Unimolecular Decomposition of Cyclic Alkyl Radicals," J. Phys. Chem. A, vol. 112, nr. 46, pp. 11598-11610, 2008.

[49] Sirjean, B., Glaude, P. A., Ruiz-Lopèz, M. F., Fournet, R., "Theoretical Kinetic Study of the Reactions of Cycloalkylperoxy Radicals," J. Phys. Chem. A, vol. 113, pp. 6924-6935, 2009.

[50] Hoyermann, K., Maarfeld, S., Nacke, F., Nothdurft, J., Olzmann, M., Wehmeyer, J., Welz, O., Zeuch, T., "Rate Coefficients for Cycloalkyl + O Reactions and Product Branching in the Decomposition of Chemically Activated Cycloalkoxy Radicals: an Experimental and Theoretical Study," Phys. Chem. Chem. Phys., vol. 12, pp. 8953-8967, 2010.

[51] Fernandes, R.X., Za´dor, J., Jusinski, L. E., Miller, J., A., Taatjes, C. A., "Formally direct pathways and low-temperature chain branching in hydrocarbon autoignition: the cyclohexyl + O2 reaction at high pressure," Phys. Chem. Chem. Phys., vol. 11, pp. 1320-1327, 2009.

[52] Dayma, G., Glaude, P. A., Fournet, R., Battin-Leclerc, F., "Experimental and Modeling Study of the Oxidation of Cyclohexene," International Journal of Chemical Kinetics, vol. 35, no. 7, pp. 273-285, 2003.

[53] Slavinskaya, N. A., Wacker, M., "Kinetic Modeling of Cyclohexane Oxidation with PAH Formation," European Combustion Symposium, Wien, April 2009.

[54] Abbasi, M., Slavinskaya, N. A., Riedel, U., "Kinetic Modeling of Cyclohexane Oxidation including PAH Formation," 7th Proceeding of the European Combustion Meeting, P1-49, Budapest 2015.

[55] Abbasi, M., Slavinskaya, N. A., Riedel, U., "Kinetic Modeling of Cyclohexane Oxidation Including PAH Formation," 55th AIAA Aerospace Sciences Meeting, Grapevine, Texas, USA, January 2017.

[56] Abbasi, M. Slavinskaya, N. A., Riedel, U., "Kinetic Modeling of Cyclohexane and n-Propylcyclohexane Oxidation with the PAH Precursor Formation," 2018 AIAA Aerospace Sciences Meeting Kissimmee, Florida, January 2018.

[57] Tsang, W. "Thermal Stability of Cyclohexane and 1- Hexene," J. Phys. Chem. Ref. Data, vol. 10, pp. 1119-1138, 1978.

[58] Slavinskaya, N. A., Frank, P., "modelling study of aromatic soot precursors formation in laminar methane and ethene flames," Combust. Flame, vol. 156, pp. 1705-1722, 2009.

[59] Chernov, V., Thomson, M., Dworkin, S. B., Slavinskaya, N., Riedel, U., "Soot Formation with C_1 and C_2 Fuels Using a Novel Chemical Mechanism for PAH Growth," Combustion and Flame, vol. 161, pp. 592-601, 2014.

[60] Orme, J. P., Curran, H. J., Simmie, J. M., "Experimental and Modeling Study of Methyl Cyclohexane Pyrolysis and Oxidation," J. Phys. Chem. A, vol. 110, pp. 114-131, 2006.

[61] Pitz ,W. J., Naik, C.V., Ní Mhaoldúin, T., Westbrook, C.K., Curran, H. J., Orme, J.P., Simmie, J. M., "Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine," Proceedings of the Combustion Institute, vol. 31, pp. 267-275, 2007.

[62] Handford-Styring, S. M., Walker, R. W., "Arrhenius Parameters for the Reaction HO_2 Between + Cyclohexane 673 and 773 K, and for H Atom Transfer in Cyclohexylperoxy Radicals," Phys. Chem. Chem. Phys., vol. 3, pp. 2043-2052, 2001.

[63] Ranzi, E., Frassoldati, A., Grana, R., Cuoci, A., Faravelli, T., Kelley, A. P., Law, C. K., "Hierarchical and Comparative Kinetic Modeling of Laminar Flame Speeds of Hydrocarbon and Oxygenated Fuels," Progress in Energy and Combustion Science, vol. 38, pp. 468-501, 2012.

[64] Bogin, G. E., Osecky, E., Ratcliff, M.A., Luecke, J., He, X., Zigler, B. T., Dean, A. M. "Ignition Quality Tester (IQT) Investigation of the Negative Temperature Coefficient Region of Alkane Autoignition," Energy & Fuels, vol. 27, pp. 1632-1642, 2013.

[65] Zhorov, Y. M., "Thermodynamics of Chemical Processes; Petrochemical synthesis, processing of petroleum, coal, and natural gas," 1st Edition, Moscow, Russia: Mir Publications, 1987.

[66] Trautz, M., and Anorg, Z., "Evaluation of Arrhenius Frequency Factor (A) by Simple Collision Theory," Chemistry, vol. 96, nr.1, 1916.

[67] Lewis, W. C. M., "Evaluation of Arrhenius Frequency Factor (A) by Simple Collision Theory Assuming Atoms and Molecules As Hard Spheres," Journal of Chemistry Socialist, vol. 113, pp. 471, 1918.

[68] Chernyi, G.G., Losev, S. A., Macheret, S. O., Potapkin, B. V. , "Physical and Chemical Processes in Gas Dynamics : Cross Sections and Rate Constants," Reston, United States : American Institute of Aeronautics & Astronautics, June 2002.

[69] Kurbatov, V.S., Silin, I. N., "New method for minimizing regular functions with constraints on parameter region," Nucl. Instrum. Methods., vol. A 345, pp. 346-350, 1994.

[70] Sokolov, S., Silin, I., .Preprint JINR D-810,“ Dubna, 1961.

[71] Fokin, L., Slavinskaya, N., Institute for High Temperatures, USSR Academy of Sciences, vol. 25, no. 1, pp. 40-45, 1987.

[72] Miyoshi, A., Tsuchiya, K., Yamauchi, N., Matsui, H., "Reactions of Atomic Oxygen (3P) with Selected Alkanes," J. Phys. Chem., vol. 98, pp. 11452-11458, 1994.

[73] Knepp, A. M., Meloni, G., Jusinski, L. E., Taatjes, C. A., Cavallotti, C., Klippenstein, S. J., "Theory, measurements, and modeling of OH and HO_2 formation in the reaction of cyclohexyl radicals with O_2," Phys. Chem. Chem. Phys., vol. 9, pp. 4315-4331, 2007.

[74] Stuckey, W. K., Heicklen, J., "Some Reactions of Oxygen Atoms. III. Cyclopropane, Cyclobutane, Cyclopentane," The Journal of Chemical Physics, vol. 46, pp. 4843, 1967.

[75] N. Cohen, "The use of transition-state theory to extrapolate rate coefficients for reactions of oh with alkanes," Int. J. Chem. Kinet. vol. 14, pp. 1339-1362, 1982.

[76] Wang, H., Dames, E., Sirjean, B., Sheen, D. A., Tango, R., Violi, A., Lai, J. Y. W., Egolfopoulos, F. N., Davidson, D. F., Hanson, R. K., Bowman, C. T., Law, C. K., Tsang, W., Cernansky, N. P., Miller, D. L., Lindstedt, R. P., "A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures," JetSurF version 2.0, 19 09 2010. [Online]. Available: http://web.stanford.edu/group/haiwanglab/JetSurF/JetSurF2.0/index.html [Accessed 30.04.2019].

[77] Wang, Z., L. Zhao, Y. Wang, H. Bian, L. Zhang, F. Zhang, Y. Li,S. M. Sarathy, F. Qi,, "Kinetics of ethylcyclohexane pyrolysis and oxidation: An experimental and detailed kinetic modeling study," Combustion and Flame, vol. 162, pp. 2873-2892, 2015.

[78] Ritter, E. R., Bozzelli, J. W., "THERM: Thermodynamic property estimation for gas phase radicals and molecules," Int. J. Chem. Kinet., vol. 23, pp.767, 1991.

[79] Benson, S. W. , Thermochemical Kinetics, New York, USA: John Wiley & Sons Ltd., 2nd Edition, 1976.

[80] Muller, C., Michel, V., Scacchi, G., Côme, G. M., "THERGAS: a computer program for the evaluation of thermochemical data of molecules and free radicals in the gas phase," J. Chim. Phys., vol. 92, pp. 1154-1178, 1995.

[81] "National Institute of Standards and Technology," [Online]. Available: http://webbook.nist.gov/chemistry/form-ser.html. [Accessed 30.04.2019].

[82] Burcat, A., Goos, E., Ruscic, B., "Ideal Gas Thermochemical Database with updates from Active Thermochemical Tables," [Online]. Available: http://garfield.chem.elte.hu/Burcat/burcat.html. [Accessed 30.04.2019].

[83] Abbasi, M., Slavinskaya, N. A., Riedel, U., "Uncertainty of Thermo-Chemical Properties of Species Related to Cyclohexane Low Temperature Oxidation," Eurasian Chemico-Technological Journal, vol. 20, pp. 263-275, 2018.

[84] Rossini, F.D., Pitzer, K. S., Arnett, R. L., Braun, R. M., and Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons & Related Compounds," Comprising the Tables of the American Petroleum Institute Research Project 44 Extant as of December 31, 1952 (Carnegie Press, Pittsburgh, 1953).

[85] Wilhoit, R. C., Chao, J., Hall, K. R., "Thermodynamic Properties of Key Organic Oxygen Compounds in the Carbon Range C_1 to C_4. Part 1. Properties of Condensed Phases," J. Phys. Chem. Ref. Data, vol. 14, nr.1, 1985, https://doi.org/10.1063/1.555747.

[86] Goldsmith, C. F., Magoon, G. R., Green, W. H., "Database of Small Molecule Thermochemistry for Combustion," J. Phys. Chem. A, vol. 116, pp. 9033-9057, 2012.

[87] Benson, S. W., Cruickshank, F. R., Golden, D. M., Haugen, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R., Walsh, R., "Additivity Rules for The Estimation of Thermochemical Properties," Chemical Reviews, vol. 69, pp. 279-324, 1969.

[88] Benson, S. W. and Buss, J. H., "Additivity Rules for the Estimation of Molecular Properties, Thermodynamic Properties," J. Chem. Phys., vol. 29 pp. 90, 1958.

[89] Luria, M. and Benson, S. W., "Heat capacities of liquid hydrocarbons. Estimation of heat capacities at constant pressure as a temperature function, using additivity rules," J. Chem.Eng. Data, vol. 22, pp. 90-100, 1977.

[90] O'Neal, H. E., Benson, S. W., "Thermochemistry of free radicals," in Free Radicals, ed. J. K. Kochi, New York, Wiley, 1973, Chapter 17.

[91] Sabbe, M. K., Saeys. M., Reyniers, M., Marin, G. B., "Group Additive Values for the Gas Phase Standard Enthalpy of Formation of Hydrocarbons and Hydrocarbon Radicals," J. Phys. Chem. A, vol. 109, pp. 7466-7480, 2005.

[92] Sabbe, M. K., Vleeschouwer, F., Reyniers, M., Waroquier, M., Marin, G. B., "First Principles Based Group Additive Values for the Gas Phase Standard Entropy and Heat Capacity of Hydrocarbons and Hydrocarbon Radicals," J. Phys. Chem. A, vol. 112, pp. 12235-12251, 2008.

[93] Cohen, N., "Revised Group Additivity Values for Enthalpies of Formation (at 298 K) of Carbon-Hydrogen and Carbon Hydrogen-Oxygen Compounds," J. Phys. Chem. Ref. Data, vol. 25, nr. 6, pp. 1411, 1996, https://doi.org/10.1063/1.555988.

[94] Khan, S. S., Yu, X., Wade, J. R., Malmgren, R. D., Broadbelt, L. J., "Thermochemistry of Radicals and Molecules Relevant to Atmospheric Chemistry: Determination of Group Additivity Values using G3//B3LYP Theory," J. Phys. Chem. A, vol. 113, pp. 5176-5194, 2009.

[95] Bhattacharya, A., Shivalkar, S., "Re-tooling Benson's Group Additivity Method for Estimation of the Enthalpy of Formation of Free Radicals: C/H and C/H/O Groups," J. Chem. Eng. Data, vol. 51, pp. 1169-1181, 2006.

[96] Domalski, E.S., Hearing, E. D., "Estimation of the Thermodynamic properties of C-H-N-O-S-Halogen Compounds at 298 K, Chemical Kinetics and Thermodynamics Division," National Institute of Standards and Technology, Gaithersburg, MD 2089-0001, 1993.

[97] Dorofeeva, O. V., Tolmach, P.I., "On the Estimation of Gas-Phase Thermodynamic Properties of Organic-Compounds," Thermonchimica Acta, vol. 219, pp. 361-364, 1993.

[98] Hansen, N., Harper, M. R., and Green. W. H., "High-temperature oxidation chemistry of n-butanol – experiments in low-pressure premixed flames and detailed kinetic modeling," Phys. Chem. Chem. Phys., vol. 13, pp. 20262-20274, 2011.

[99] Joback, K. G., Reid. R. C., "Estimation of Pure-Component Properties from Group-Contributions," Chem. Eng. Comm., vol. 57, pp. 233-243, 1987.

[100] Cohen. N., Benson. S. W., "Estimation of heats of formation of organic compounds by additivity methods," Chem. Rev., vol. 93, pp. 2419-2438, 1993.

[101] Lay, T., H., Yamada, T., Tsai, P., L., Bozzelli, J., W., "Thermodynamic Parameters and Group Additivity Ring Corrections for Three- to Six-Membered Oxygen Heterocyclic Hydrocarbons," J. Phys. Chem. A, vol.101, pp. 2471-2477, 1997.

[102] Sheng. C. Y., Bozelli. J. W., Dean. A. M., Chang. A. Y., "Detailed Kinetics and Thermochemistry of C2H5 + O2: Reaction Kinetics of the Chemically-Activated and Stabilized CH3CH2OO• Adduct," J. Phys. Chem. A, vol. 106, pp. 7276-7293, 2002.

[103] Dorofeeva, O. V., "Ideal gas thermodynamic properties of oxygen heterocyclic compounds, Part 2, Six-membered, seven-membered and eight-membered rings," Thermochimica Acta, vol. 200, pp. 121-150, 1992.

[104] Da Silva, G., Bozzelli, J. W., "Enthalpies of Formation, Bond Dissociation Energies, and Molecular Structures of the n-Aldehydes (Acetaldehyde, Propanal, Butanal, Pentanal, Hexanal, and Heptanal) and Their Radicals," J. Phys. Chem. A, vol. 110, pp. 13058-13067, 2006.

[105] Holmes, J. L., Lossing, F. P., Mayer, P. M., "Heats of formation of oxygen-containing organic free radicals from appearance energy measurements," J. Am. Chem. Soc., vol. 113, nr. 26, pp. 9723-9728, 1991.

[106] William H. Green, Richard H. West, and the RMG Team, "Reaction Mechanism Generator- "RMG"," [Online]. Available: https://reactionmechanismgenerator.github.io/RMG-Py/index.html. [Accessed 30.04.2019].

[107] Sumathi, R., Green, W. H., "Oxygenate, oxyalkyl and alkoxycarbonyl thermochemistry and rates for hydrogen abstraction from oxygenates," Jr. Phys. Chem. Chem. Phys., vol. 5, pp. 3402-3417, 2003.

[108] B. Ruscic, Active Thermodynamic Tables : version Alpha 1.110 of the Core (Argonne), Thermochemical Network, 04.02.2011.

[109] Baulch, D. L., Bowman, C. T., Cobos, C. J., Cox, R. A., Just, T., Kerr, J. A., Pilling, M. J., Stocker, D., Troe, J., Tsang, W., Walker, R. W., Warnatz, J., "Evaluated Kinetic Data for Combustion Modeling," J. Phys. Chem. Ref. Data, vol. 34, nr. 3, pp.757-1397, 2005.

[110] M. Frenklach, A. Packard, Z. M. Djurisic, D. M. Golden, C. T. Bowman, W. H. Green, G. J. McRae, T. C. Allison and G. J. Rosasco, "PrIMe," 2007. [Online]. Available: https://prime.cki-know.org/. [Accessed 1 9 2017] Mirrored at http://primekinetics.org/ [Accessed 30.04.2019].

[111] Berkowitz, J., Ellison, G. B., Gutman, D., "Three methods to measure RH bond energies," J. Phys. Chem., vol. 11, pp. 2744-2765, 1994.

[112] CHEMKIN/CHEMKIN-PRO Input Manual, San Diego, U.S.: CHEMKIN-PRO 15101, Reaction Design, 2010.

[113] Kee,R. J.,Rupley, F. M. , Miller, J. A., Coltrin, M. E., Grcar,J. F., Meeks, E., Moffat, H. K., Lutz,A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans,G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, et. al. , CHEMKIN Collection, Release 3.6, San Diego, CA, U.S.: Reaction Design, Inc., 2000.

[114] Dixon-Lewis, G., "Flame structure and flame reaction kinetics. II. Transport phenomena in multi-component systems," Proceedings of the Royal Society A. 304, pp. 111-135 .1968.

[115] Warnatz, J., "Numerical Methods in Flame Propagation," Ed. by Peters, N. and Warnatz, J., Wiesbaden, Germany: Friedr. Vieweg and Sohn, 1982.

[116] Kee, R. J., Warnatz, J. and Miller, J. A., "Fortran Computer Code Package for the Evaluation of Gas-Phase Viscosities, Conductivities, and Diffusion Coefficients," Sandia National Laboratories Report, Sandiago, CA, U.S., SAND83-8209, 1983.

[117] Moss, G.P., Smith, P.A.S., Tavernier, D., "Glossary of Class Names of Organic Compounds and Reactive Intermediates Based on Structure," Pure and Applied Chemistry , vol. 67, nr. 8-9, pp. 1307–1375, doi:10.1351/pac199567081307, 1995.

[118] Ried, R.C., Prausnitz, J.M., Sherwood, T.K., "The Properties of Gases and Liquids," 3rd Ed., McGraw-Hill-ISBN 0-07-051790-8, pp. 439-456, 1997.

[119] Pitzer, K. S., Lippmann, D. Z., Curl, R. F., Huggins,C. M., Petersen, D. E., J. Am. Chem.Soc., vol. 77, pp. 3433, 1955.

[120] Tasi, G., Mizukamia, F., Palinko., I., "Analysis of permanent electric dipole moments of aliphatic hydrocarbon molecules," Journal of Molecular Structure (Theochem), vol. 401, pp. 21-27, 1997.

[121] Gokel, G. W., Dean's handbook of organic chemistry, 2nd Ed., New York, U.S.: McGraw-Hill, ISBN 0-07-137593-7, 2004.

[122] Bosque, R., and Sales, J., "Polarizabilities of Solvents from the Chemical Composition," J. Chem. Inf. Comput. Sci., vol. 42, pp. 1154-1163, 2002.

[123] Stout, J. M., Dykstra, C. E., "Static Dipole Polarizabilities of Organic Molecules, Ab Initio Calculations and a Predictive Model," J. Am. Chem. Soc., vol. 117, pp. 5127-5132, 1995.

[124] Kier, L. B., Hall, L. H., "Molecular Connectivity in Structure-Activity Analysis," Research Studies Press, Letchworth, England: Research Studies Press: Wiley, 1986.

[125] Hall, L. B., Aaserud, D., "Structure-Activity Models for Molar Refraction of Alkylsilanes Based on Molecular Connectivity," Quant. Struct.-Act. Relat., vol. 8, pp. 296-304, 1989.

[126] Katritzky, A. R., Sild, S., Karelson, M., "General Quantitative Structure Property Relationship Treatment of the Refractive Index of Organic Compounds," J. Chem. Inf. Comput. Sci., vol. 38, pp.840-844, 1998.

[127] Katritzky, A. R., Sild, S., Karelson, M., "Correlation Prediction of the Refractive Indices by QSPR," J. Chem. Inf. Comput. Sci., vol. 38, pp. 1171-1176, 1998.

[128] Cocchi, M., Benedetti, P. G., Seeber, R., Tassi, L., Ulrici, A., "Development of Quantitative Structure-Property Relationships Using Calculated Descriptors for the Prediction of the Physicochemical Properties of a Series of Organic Solvents," J. Chem. Inf. Comput. Sci., vol. 39, pp.1190-1203, 1999.

[129] Partington, J. R., "An Advanced Treatise on Physical Chemistry," London, U.K., Longmans, vol. 4, 1953.

[130] Applequist, J., Carl, J. R., Fung, K. K., "An Atom Dipole Interaction Model for Molecular Polarizability, Application to Polyatomic Molecules and Determination of Atomic Polarizabilities," J. Am. Chem. Soc., vol. 94, pp. 2952-2960, 1972.

[131] Brau, C. C., and Jonkman, R. M. , Journal of Chemical Physics, vol. 52, pp. 447, 1970.

[132] Parker, J. G., Physics of Fluids, vol. 2, pp. 449, 1959.

[133] Widom, B., "Rotational Relaxation of Rough Spheres," J. Chem. Phys., vol. 32, no. 3, pp. 913-923, 1960.

[134] Lambert, D., Vibrational and rotational relaxation in Gases, U.K.: Oxford University Press: ISBN 0-19-855605-5, 1977.

[135] Leipertz, A., Kiefer, J., "Soot and Soot Diagnostics by Laser-Induced Incandescence," in Handbook of Combustion, Hoboken, NJ, Wiley-VCH, pp. 403-423, 2010.

[136] "Kintech Lab Ltd. Chemical Workbench®," [Online]. Available: http://www.kintechlab.com/.

Appendices

Appendix I

Reaction mechanism

```
ELEMENTS   H   O   C   N   AR  HE END
SPECIES
N2             AR             HE             O2             O
H              HO2            OH             H2             H2O2
H2O            C              CO2            CO             CH
HCO            CH2            CH2(S)         CH2O           CH3
CH3O           CH2OH          CH4            CH3OH          C2
C2H            HCCO           C2H2           CH2CO          C2H3
CH2HCO         CH3CO          C2H4           CH3CHO         C2H5
C2H5O2         CH2CH2OH       CH3CH2O        CH3CHOH       CH2CHOO
C2H6           C2H5O2H        C2H5OH         C2H3OH         CH3O2
CH3O2H         CH2CH2O2H      O2C2H4OH      C2H4O2OH
C3H2            H2CCCH        sC3H5OOH     pC3H5OOH  C2H5CHO
C4H            C4
C3H4           C3H5           C3H6           nC3H7     iC3H7
C3H8           C4H2           H2CCCCH        C4H4     i-C4H5
C4H6           nC4H7          C4H8           iC4H8
nC4H9          iC4H9          tC4H9    C3H5O
sC4H9          nC4H10
C4H8OOO2H      C4H9OO   C4H8OOH    C4H8O  C4H7O    C4H8O3
C4H9OOH
C5H11  C5H10 C5H9 C5H8
iC6H13   iC7H15  iC8H17 iC4H7 iC5H11  iC5H10
aC6H12 C6H11  C6H13 iC6H12 iC6H11
aC7H14    cC7H14    C6H10
C7H16     C7H13     C7H15O2   C7H15OO  C7H15O4  C7H15O
C7H15     C5H9O     C7H14O3
aC8H17    iC8H16    dC8H17
iC8H15    iC8H18    C8H16O3   C6H12CHO   C8H17
cC8H17OO  cC8H17O2  cC8H17O4
cyC6H11OOH cyC6H9O   C5H10CHO  C3H6CHO  C2H3CHO  C3H5CHO C2H4CHO
cyC6H12 cyC6H11  cyC6H10   cyC6H10OOH     cyC6H9   CH2CHO
cyC6H11OO  cyC6H10OH  cyOOC6H10OOH  C5H9CHO C3H4O cyC6H8 cyC6H11O
cyC5H7  cyC6H7 cyC6H10Oa cyC6H10Ob  cyC6H10Oc cyC6H10Od C6H10O
cyC6H9OO   cyC6H8OOH   cyOOHC6H9OOH cyOC6H9OOH cyOC6H9O
!!!PropylCHX!!!!!!!!
cyC9H18   cyC9H17A cyC9H17B  cyC9H17E  cyC8H15  cyC8H14 cyC7H13  cyC7H12
cyC9H17OOA cyC9H17OOB cyC9H17OOE cyC9H17OA cyC9H17OB cyC9H17OE
cyC9H16OOHA cyC9H16OOHB  cyC9H16OOHC  cyC9H16OOHD
cyC9H16OOHE  cyC9H16OB  cyC9H16OE
cyOOC9H16OOHA  cyOOC9H16OOHB cyOOC9H16OOHC  cyOOC9H16OOHD cyOOC9H16OOHE
cyOC9H15OOHA cyOC9H15OOHB cyOC9H15OOHC cyOC9H15OOHD cyOC9H15OOHE
cyC9H16B cyC9H16E
A1             A1-            C6H5OH    C6H5O     C5H5      C5H6
A1C2H     C7H8
A1C2H3    A1C2H3*   n-C8H7    C7H7      A1C2H-
A2       A2-       INDENE    INDENYL
P2        P2-
A2C2H*    A2R5      A2C2H     A2R5-     A3        A3-
A4        A4-       C18H12    C18H11    A3C2H     A3C2H*
```

```
C6H2      C8H2      C6H       C8H
A4C2H     A4C2H*    BAPYR*S   BGHIF
BAPYR     A2CH3     A2CH2     A3CH3     A3CH2
END

REACTIONS  MOLES  KELVINS

!!!!!!!!!!!!!!!!!!!!!!!!!!INP_MECH_22.09.2017!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
REACTIONS  MOLES  KELVINS
C2H3+O2=CH2CHOO         1.650E+13  -0.02   -430.0
CH2CHOO+OH=C2H3OH+O2    2.0E15     -0.600  0.0
CH2CHOO+OH=CH2HCO+HO2   4.0E+11    0.600   0.0
CH2CHOO=CH2HCO+O        5.22E+29   -4.71   21170.0
CH2CHOO+H=CH2HCO+OH     9.6E+13    0.000   0.0
CH2CHOO=CH2CO+OH        1.55E+24   -3.87   24990.0
CH2CHOO=CH2O+HCO        0.40E+20   -2.29   15085.0
CH2CHOO=CH2O+H+CO       1.19E+20   -2.29   15085.0
CH2CHOO=CO+CH3O         1.16E-01    3.16   9210.0
CH2CHOO=CO2+CH3         6.03E-03    3.46   8710.0

!****************************** O ****************************************
!*************************************************************************
2O+M=O2+M               5.400E+13  0.00    -899.7
   H2/2.5/ H2O/16.25/ CO/1.88/ CO2/3.75/ AR/0.87/ HE/0.87/
!****************************** HO2 ***************************************
!*************************************************************************
H+O2(+H2O)=HO2(+H2O)    9.020E+12  0.20    0.0
  TROE /8.000E-01  1.000E-30  1.000E+30 /
  LOW /3.670E+19  -1.000       0./
H+O2(+N2)=HO2(+N2)      4.660E+12  0.44    0.0
  TROE /5.000E-01  1.000E-30  1.000E+30 /
  LOW /1.750E+19  -1.230       0./
H+O2(+O2)=HO2(+O2)      4.660E+12  0.44    0.0
  TROE /5.000E-01  1.000E-30  1.000E+30 /
  LOW /5.690E+18  -1.090       0./
H+O2(+AR)=HO2(+AR)      4.660E+12  0.44    0.0
  TROE /5.000E-01  1.000E-30  1.000E+30 /
  LOW /7.430E+18  -1.200       0./
H+O2(+HE)=HO2(+HE)      4.660E+12  0.44    0.0
  TROE /5.000E-01  1.000E-30  1.000E+30 /
  LOW /6.130E+18  -1.200       0./
H+O2(+M)=HO2(+M)        4.660E+12  0.44    0.0
  H2/1.5/ O2/0/ H2O/0/ CO2/1.06/ N2/0/ AR/0/
  TROE /5.000E-01  1.000E-30  1.000E+30 /
  LOW /1.750E+19  -1.230       0./
!****************************** OH ****************************************
!*************************************************************************
O+HO2=O2+OH             1.630E+13  0.00    -224.0
H+HO2=2OH               4.000E+14  0.00     700.0
H+O+M=OH+M              7.730E+18  -1.00    0.0
 H2/2.5/ CH4/7.5/ C2H6/7.5/ H2O/16.25/ CO/1.88/ CO2/3.75/ AR/0.87/ HE/0.87/
H+O2=OH+O               1.900E+14  -0.10   7560.0
!********************** H2 ****************************************************
!*************************************************************************
H+HO2=H2+O2             2.000E+14  0.00    1030.0
H2+O=OH+H               8.790E+14  0.00    9650.0
DUPLICATE
H2+O=OH+H               3.820E+12  0.00    4000.0
DUPLICATE
```

```
2H+M=H2+M               7.470E+17  -1.00    0.0
   H2/0/ H2O/0/ CO/1.88/ CO2/3.75/ H/0/ N2/0/ AR/0/ HE/0.87/
3H=H2+H                 3.200E+15  0.00     0.0
2H+N2=H2+N2             5.400E+18  -1.30    0.0
2H+H2=2H2               1.000E+17  -0.60    0.0
2H+AR=H2+AR             6.530E+17  -1.00    0.0
H2+O2=2OH               2.400E+13  0.47     35121.0
!********************** H2O2 ********************************************
!************************************************************************
2HO2=H2O2+O2            1.320E+11  0.00     -820.3
DUPLICATE
2HO2=H2O2+O2            4.220E+14  0.00     6030.8
DUPLICATE
H2O2+O=OH+HO2           8.430E+11  0.00     2000.0
H2O2+H=HO2+H2           1.690E+12  0.00     1889.6
OH+OH(+M)=H2O2(+M)      1.590E+13  0.00     0.0
   H2/2.5/ CO/1.875/ CO2/3.75/ H2O/0.0/ AR/0.875/
   LOW  /2.4E+19  -0.8     0.00 /
   TROE /1 1 1 243/
OH+OH(+H2O)=H2O2(+H2O) 1.590E+13  0.00     0.0
   LOW  /1.40E+18    0.0     0.00 /
   TROE /1 1 1 243/
!********************** H2O *********************************************
!************************************************************************
H2O2+OH=H2O+HO2         1.930E+12  0.00     215.0
DUPLICATE
H2O2+OH=H2O+HO2         1.640E+18  0.00     14800.0
DUPLICATE
OH+HO2=H2O+O2           2.890E+13  0.00     -250.0
DUPLICATE
OH+HO2=H2O+O2           9.270E+15  0.00     8810.0
DUPLICATE
2OH=O+H2O               3.350E+04  2.42     -970.0
H2O2+H=OH+H2O           1.020E+13  0.00     1800.6
H+HO2=H2O+O             1.440E+12  0.00     0.0
H+OH(+AR)=H2O(+AR)      2.511E+13  0.23     -57.5
  TROE /2.800E-01  1.000E+33  1.000E+33 /
  LOW /3.114E+20  -1.510     185./
H+OH(+M)=H2O(+M)        2.511E+13  0.23     -57.5
  H2/2.5/ H2O/16.39/ CO/1.88/ CO2/3.75/ AR/0/ HE/0.87/
  TROE /2.700E-01  1.000E+33  1.000E+33 /
  LOW /4.533E+21  -1.810     251./
OH+H2=H2O+H             2.160E+08   1.52    1740.0
2H+H2O=H2+H2O           1.000E+19  -1.00    0.0
!********************** CO **********************************************
!************************************************************************
C+OH=CO+H               5.000E+13  0.00     0.0
O2+C=CO+O               1.200E+14  0.00     2009.9
CO+HO2=CO2+OH           1.150E+05  2.28     8775.0
CO+O(+M)=CO2(+M)        1.362E+10  0.00     1242.0
LOW /1.173E+24   -2.79    2095.0   /
H2/2.0/ H2O/12/ CO/1.75/ CO2/3.6/ AR/0.7/ HE/0.7/
CO+OH=CO2+H             1.010E+11  0.00     30.0
DUPLICATE
CO+OH=CO2+H             9.030E+11  0.00     2300.0
DUPLICATE
CO+OH=CO2+H             1.010E+13  0.00     8050.0
DUPLICATE
O2+CO=CO2+O             1.260E+13  0.00     23682.9
```

```
!********************** CH ************************************************
!**************************************************************************
H+CH=C+H2               8.430E+12  0.00    0.0
CH+O=CO+H               3.970E+13  0.00    0.0
O2+CH=CO2+H             1.660E+13  0.00    0.0
O2+CH=CO+OH             1.660E+13  0.00    0.0
!********************** HCO ***********************************************
!**************************************************************************
CH+OH=HCO+H             3.000E+13  0.00    0.0
CO2+CH=HCO+CO           3.430E+12  0.00    345.2
HCO+M=H+CO+M            4.750E+11  0.66    7485.0
H2/2.5/ CO/1.87/ CO2/3.75/ H2O/16.25/ AR/0.87/ HE/0.87/
HCO+HO2=CO2+OH+H        3.000E+13  0.00    0.0
HCO+OH=H2O+CO           1.020E+14  0.00    0.0
HCO+O=CO2+H             3.010E+13  0.00    0.0
HCO+O=CO+OH             3.010E+13  0.00    0.0
HCO+H=CO+H2             9.000E+13  0.00    0.0
HCO+O2=OH+CO2           0.200E+10  0.68    -236.0
HCO+O2=HO2+CO           2.500E+10  0.68    -236.0
!********************** CH2 ***********************************************
!**************************************************************************
CH2+O=CO+H2             4.800E+13  0.00    0.0
CH2+O=CO+2H             7.200E+13  0.00    0.0
H+CH2=CH+H2             6.020E+12  0.00    -899.7
O2+CH2=CO+H2O           1.480E+12  0.00    750.5
O2+CH2=CO+OH+H          8.150E+12  0.00    750.5
O2+CH2=CO2+2H           5.430E+12  0.00    750.5
O2+CH2=CO2+H2           5.430E+12  0.00    750.5
!********************** CH2(S)*********************************************
!**************************************************************************
CH2(S)+M=CH2+M          1.510E+13  0.00    0.0
 CH4/0.48/C2H2/3.2/C2H4/1.6/C2H6/1.44/O2/0.4/H2O/6.5/CO/0.75/CO2/1.5/AR/0.2/
H+CH2(S)=CH2+H          2.000E+14  0.00    0.0
O2+CH2(S)=CO+OH+H       3.130E+13  0.00    0.0
!********************** CH2O **********************************************
!**************************************************************************
2HCO=CH2O+CO            3.010E+13  0.00    0.0
CH2+OH=CH2O+H           1.810E+13  0.00    0.0
HCO+H(+M)=CH2O(+M)      1.090E+12  0.48    -130.0
  LOW/1.350E+024  -2.570  712.5/
  TROE/  7.824E-001  2.710E+002  2.755E+003  6.570E+003/
  H2/2.00/ H2O/6.00/AR/0.70/ CO/1.50/CO2/2.00/CH4/2.00/C2H6/3.00/HE/0.70/
CO+H2(+M)=CH2O(+M)      4.300E+07  1.50    39800.0
  LOW/5.070E+027    -3.420   42174.0/
  TROE/  9.320E-001  1.970E+002  1.540E+003  1.030E+004/
  H2/2.00/ H2O/6.00/AR/0.70/CO/1.50/CO2/2.00/CH4/2.00/C2H6/3.00/HE/0.70/
CH2O+HO2=H2O2+HCO       3.010E+12  0.00    6580.5
CH2O+OH=HCO+H2O         3.430E+09  1.18    -224.9
CH2O+O=HCO+OH           4.160E+11  0.57    1390.4
CH2O+CH=CH2+HCO         9.640E+13  0.00    -259.8
CH2O+H=HCO+H2           1.260E+08  1.62    1089.7
CO2+CH2=CH2O+CO         2.350E+10  0.00    0.0
O2+CH2=CH2O+O           4.200E+12  0.00    750.5
O2+CH2O=HCO+HO2         6.020E+13  0.00    20460.7
!********************** CH3 ***********************************************
!**************************************************************************
CH3+H=CH2+H2            7.000E+13  0.00    7500.0
CH3+M=CH2+H+M           2.910E+16  0.00    45602.6
 CH4/3/ C2H6/3/ O2/0.4/ H2O/6.5/ CO/0.75/ CO2/1.5/ AR/0.4/
```

```
CH3+OH=CH2(S)+H2O      7.230E+13  0.00    1400.0
CH3+O=CH2O+H           4.230E+13  0.00    0.0
CH2+HCO=CH3+CO         1.810E+13  0.00    0.0
O2+CH3=CH2O+OH         1.210E+12  0.00    7094.8
H2+CH2(S)=CH3+H        7.230E+13  0.00    0.0
!********************** CH3O ********************************************
!************************************************************************
CH3O+CO=CH3+CO2        1.570E+13  0.00    5940.0
CH3O+HO2=CH2O+H2O2     3.010E+11  0.00    0.0
CH3O+H=CH2(S)+H2O      2.620E+14  -0.20   535.0
CH2O+H(+M)=CH3O(+M)    1.080E+11  0.50    1300.0
  H2/2/CH4/2/ C2H6/3/H2O/6/CO/1.5/CO2/2/
  TROE /7.580E-01  9.400E+01  1.555E+03  4.200E+03 /
  LOW /2.200E+30  -4.800    2780./
CH3+OH=CH3O+H          5.700E+12  -0.23   6900.0
CH3+O2=CH3O+O          2.100E+13  0.00    16340.0
OH+CH3O=CH2O+H2O       1.810E+13  0.00    0.0
O+CH3O=CH2O+OH         1.810E+12  0.00    0.0
CH3+HO2=CH3O+OH        1.800E+13  0.00    0.0
H+CH3O=CH2O+H2         1.810E+13  0.00    0.0
O2+CH3O=CH2O+HO2       2.170E+10  0.00    880.4
!********************** CH2OH *******************************************
!************************************************************************
CH2OH+HCO=2CH2O        1.800E+14  0.00    0.0
CH2OH+CH2=CH2O+CH3     1.200E+12  0.00    0.0
CH2OH+H=CH2(S)+H2O     3.280E+13  -0.10   305.0
CH3O+H=H+CH2OH         4.150E+07  1.60    812.0
CH2O+H(+M)=CH2OH(+M)   5.400E+11  0.50    1800.0
  H2/2/CH4/2/C2H6/3/H2O/6/CO/1.5/CO2/2/
  TROE /7.187E-01  1.030E+02  1.291E+03  4.160E+03 /
  LOW /1.270E+32  -4.820    3265./
OH+CH2OH=CH2O+H2O      2.410E+13  0.00    0.0
O+CH2OH=CH2O+OH        9.030E+13  0.00    0.0
H+CH2OH=CH2O+H2        1.580E+13  0.00    0.0
H+CH2OH=CH3+OH         1.020E+13  0.00    0.0
O2+CH2OH=CH2O+HO2      1.570E+15  -1.00   0.0
!********************** CH4 *********************************************
!************************************************************************
CH3O+CH3=CH2O+CH4      2.410E+13  0.00    0.0
CH2OH+CH3=CH2O+CH4     1.400E+13  0.00    0.0
CH4+HO2=CH3+H2O2       4.480E+12  0.00    12615.0
H+CH3(+M)=CH4(+M)      1.000E+16  -0.50   263.0
  CH4/3/C2H6/3/O2/0.4/H2O/6.5/CO/0.75/CO2/1.5/AR/0.2/
  TROE /7.830E-01  7.400E+01  2.941E+03  6.964E+03 /
  LOW /1.700E+33  -4.760    1220./
CH3+HCO=CH4+CO         1.200E+14  0.00    0.0
CH2O+CH3=CH4+HCO       7.830E-08  6.10    989.9
CH4+OH=CH3+H2O         1.570E+07  1.83    1400.0
CH4+O=CH3+OH           7.230E+08  1.56    4269.9
CH4+CH2(S)=2CH3        7.000E+13  0.00    0.0
CH4+CH2=2CH3           4.300E+12  0.00    5051.7
CH4+H=CH3+H2           6.600E+08  1.60    5420.0
CH4+C=CH+CH3           5.000E+13  0.00    12085.6
CH4+O2=CH3+HO2         3.970E+13  0.00    28631.2
!********************** CH3OH *******************************************
!************************************************************************
CH3OH+O2=CH2OH+HO2     2.050E+13  0.00    22542.0
CH3OH+O=CH3O+OH        1.000E+13  0.00    2356.4
CH3OH+O=CH2OH+OH       3.880E+05  2.50    1551.7
```

```
CH3OH+M=CH2(S)+H2O+M   7.000E+15  0.00    33437.9
CH2OH+CH3O=CH3OH+CH2O  2.400E+13  0.00    0.0
CH2OH+CH2O=CH3OH+HCO   5.500E+03  2.80    2950.0
CH2OH+HCO=CH3OH+CO     1.200E+14  0.00    0.0
2CH2OH=CH3OH+CH2O      4.800E+12  0.00    0.0
CH3O+CH2O=CH3OH+HCO    1.100E+11  0.00    1500.0
2CH3O=CH3OH+CH2O       6.000E+13  0.00    0.0
CH3O+HCO=CH3OH+CO      1.100E+11  0.00    1500.0
CH3OH+CH3=CH3O+CH4     1.000E+01  3.45    4020.0
CH3OH+CH3=CH2OH+CH4    2.000E+01  3.45    4020.0
CH3OH+CH2=CH3O+CH3     1.440E+01  3.10    3450.0
CH3OH+CH2=CH2OH+CH3    3.190E+01  3.20    3600.0
CH3OH+CH2(S)=CH2OH+CH3 1.200E+12  0.00    0.0
CH3OH+OH=CH3O+H2O      1.100E+06  1.92    -144.0
CH3OH+OH=CH2OH+H2O     5.100E+06  1.92    -144.0
CH3OH+H=CH3O+H2        1.700E+09  1.24    2260.0
CH3OH+H=CH2OH+H2       1.700E+09  1.24    2260.0
CH3O+H(+M)=CH3OH(+M)   2.430E+12  0.50    25.0
  H2/2/CH4/2/C2H6/3/H2O/6/CO/1.5/CO2/2/
  TROE /7.000E-01  1.000E+02  9.000E+04  1.000E+04 /
  LOW /4.660E+41  -7.440   14080./
CH2OH+H(+M)=CH3OH(+M)  1.060E+12  0.50    43.0
  H2/2/CH4/2/C2H6/3/H2O/6/CO/1.5/CO2/2/
  TROE /6.100E-01  1.000E+02  9.000E+04  1.000E+04 /
  LOW /4.360E+31  -4.650    2540./
CH3+OH(+M)=CH3OH(+M)   6.000E+13  0.00    0.0
  H2/2/CH4/2/C2H6/3/H2O/6/CO/1.5/CO2/2/
  TROE /8.200E-01  2.000E+02  1.438E+03 /
  LOW /1.595E+44  -8.200       0./
CH3OH+CH3O2= CH3O +CH3O2H      1.810E+12 0.00  0.671E+04
!************************ CH3O2 ***************************************
!**********************************************************************
CH3+O2(+M)<=>CH3O2(+M)         7.812E+09  0.900   0.0
LOW/6.850E+024    -3.000       0.0/
TROE/6.000E-001  1.000E+003  7.000E+001  1.700E+003/
CH3O2+CH3 = CH3O +CH3O         7.500E+12  0.00    -0.500E+03
CH3O2+CH3O2 = CH2O+CH3OH+O2    3.110E+14  -1.61   -0.551E+03
CH3O2+CH3O2 = O2+CH3O +CH3O    1.400E+16  -1.61   0.980E+03
CH3O2+H = CH3O +OH             9.600E+13  0.00    0.000E+00
CH3O2+O = CH3O +O2             3.600E+13  0.00    0.000E+00
CH3O2+OH = CH3OH+O2            6.000E+13  0.00    0.000E+00
CH3O2+CH2O=CH3O+OH+HCO         2.000E+12  0.00    5.873E+03
!************************** C2H ***************************************
!**********************************************************************
C2H+H=C2+H2                    1.000E+12  0.00    0.0
C2H+OH=CH2+CO                  1.810E+13  0.00    0.0
C2H+O=CH+CO                    1.000E+13  0.00    0.0
C+CH2=C2H+H                    5.000E+13  0.00    0.0
O2+C2H=CO2+CH                  9.050E+12  0.00    0.0
O2+C2H=CO+HCO                  2.450E+12  0.00    0.0
!********************** HCCO **************************************
!**********************************************************************
C2H+OH=HCCO+H                  2.000E+13  0.00    0.0
CH2+HCCO=C2H+CH2O              1.000E+13  0.00    1006.7
H+HCCO=CH2+CO                  0.420E+14  0.00    0.0
O2+C2H=HCCO+O                  4.550E+12  0.00    0.0
CO+CH=HCCO                     2.770E+11  0.00    -860.0
HCCO+O=H+2CO                   9.640E+13  0.00    0.0
HCCO+OH=CH2O+CO                1.000E+13  0.00    0.0
```

```
HCCO+OH=2HCO                    1.000E+13  0.00    0.0
HCCO+O2=CO2+CO+H                4.780E+12  -0.142  575.0
HCCO+O2=HCO+CO+O                2.180E+02  2.692   1770.0
HCCO+O2=2CO+OH                  1.910E+11  -0.020  511.0
!********************** C2H2 ********************************************
!************************************************************************
!!!!!!!!!!!!!!!!!!!!H2CC!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
C2H+H(+M)= C2H2(+M)             5.000E+17  -1.00   00.00
  TROE /0.6464E+00  1.320E+02  1.315E+03  5.566E+03 /
  LOW /3.750E+34   -4.000     950./
  CH4/2/C2H6/3/H2/2.0/H2O/6.0/CO/1.5/CO2/2.0/AR/0.7/
C2H2+O2=CH2O+CO                 4.600E+15  -0.54   22514.0
C2H2+O2=HCCO+OH                 2.000E+07  1.5     15050.0
C2H2+OH=CH2CO+H                 7.530E+06  1.55    1060.00
C2H2+OH=CH3+CO                  1.230E+09  0.73    1298.0
C2H2+OH=C2H+H2O                 2.600E+06  2.4     8586.0
C2H2+O<=>CH2+CO                 1.750E+8   1.400   1110.0
C2H2+O<=>HCCO+H                 1.600E+9   1.400   1110.0
C2H2+O<=>C2H+OH                 4.630E+19  -1.410  14485.0
CH2OH+C2H=CH2O+C2H2             4.800E+13  0.00    0.0
CH3OH+C2H=CH3O+C2H2             1.200E+12  0.00    0.0
CH3OH+C2H=CH2OH+C2H2            6.000E+12  0.00    0.0
C2H2+HO2=>CH2+CO+OH             6.090E+09  0.00    3974.0
2HCCO=C2H2+2CO                  1.000E+13  0.00    0.0
2CH2=C2H2+2H                    1.080E+14  0.00    400.5
2CH2=C2H2+H2                    1.200E+13  0.00    400.5
CH+HCCO=C2H2+CO                 5.000E+13  0.00    0.0
CH+CH2=C2H2+H                   4.000E+13  0.00    0.0
C+CH3=C2H2+H                    5.000E+13  0.00    0.0
!C2H2+OH=C2H+H2O                6.000E+13  0.00    6499.9
!C2H2+OH=C2H+H2O                3.370E+07  2.00    7045.0
C2H2+CH=C2H+CH2                 3.010E+13  0.00    -25.3
C2H2+CH=H2CCCH                  3.010E+13  0.00    -25.3
C2H2+CH=C3H2+H                  3.010E+13  0.00    -25.3
C2H2+H=H2+C2H                   2.001E+10  1.64    15250.0
C2H2+O2=C2H+HO2                 1.200E+13  0.00    37527.1
CH4+C2H=CH3+C2H2                1.810E+12  0.00    0.0
!********************** CH2CO *******************************************
!************************************************************************
CH2CO+O2=CH2O+CO2               1.000E+08  0.00    0.0
CH2CO+M=CH2+CO+M                6.570E+15  0.00    28990.9
  CH4/3/C2H6/3/O2/0.4/H2O/6.5/CO/0.75/CO2/1.5/AR/0.2/
CH2CO+OH=CH2OH+CO               4.680E+12  0.00    0.0
CH2CO+OH=CH3+CO2                2.520E+12  0.00    0.0
CH2CO+O=2HCO                    2.520E+11  0.00    679.6
CH2CO+O=HCO+H+CO                2.520E+11  0.00    679.6
CH2CO+O=CH2O+CO                 4.580E+11  0.00    679.6
CH2CO+O=CH2+CO2                 1.330E+12  0.00    679.6
CH2CO+H=CH3+CO                  1.810E+13  0.00    1699.5
CH2CO+H=CH2HCO                  4.010E+13  1.43    1322.0
CH2CO+H=CH3CO                   2.010E+12  1.61    3045.5
!********************** C2H3 ********************************************
!************************************************************************
CH2OH+C2H2=CH2O+C2H3            7.200E+11  0.00    4500.0
C2H3+CH3=C2H2+CH4               3.920E+13  0.00    0.0
C2H3+HO2=>CH3+CO+OH             3.000E+13  0.00    0.0
C2H3+O2=CH2O+HCO                9.000E+16  -1.39   510.0
C2H3+O2=C2H2+HO2                1.120E+14  -0.83   1278.6
C2H3+OH=C2H2+H2O                5.000E+12  0.00    0.0
```

```
C2H3+O=CO+CH3                   3.000E+13  0.00    0.0
C2H+C2H3=2C2H2                  1.900E+13  0.00    0.0
CH2+HCCO=C2H3+CO                3.000E+13  0.00    0.0
CH2+C2H3=C2H2+CH3               1.810E+13  0.00    0.0
CH+C2H3=CH2+C2H2                5.000E+13  0.00    0.0
CH+CH3=C2H3+H                   3.000E+13  0.00    0.0
H+C2H3=C2H2+H2                  1.200E+13  0.00    0.0
C2H2+H(+M)=C2H3(+M)             8.430E+12  0.00    1300.2
  CH4/3/C2H6/3/O2/0.4/H2O/6.5/CO/0.75/CO2/1.5/AR/0.35/
  TROE /1.000E+00  1.000E+00  1.000E+00  1.231E+03 /
  LOW /3.430E+18   .000     740./
!********************** CH2HCO ******************************************
!****************************************************************************
C2H3+O2=CH2HCO+O                7.000E+13  -0.61   2631.5
CH2HCO+CH=C2H3+HCO              1.000E+14  0.00    0.0
CH2HCO+OH=CH2OH+HCO             1.000E+13  0.00    0.0
CH2HCO+OH=CH2CO+H2O             2.000E+13  0.00    0.0
CH2HCO+O=CH2O+HCO               5.000E+13  0.00    0.0
CH2HCO+H=CH3+HCO                1.000E+14  0.00    0.0
CH2HCO+O2=CH2O+OH+CO            2.200E+11  0.00    750.0
CH2HCO+M=CH3+CO+M               2.000E+16  0.00    21000.0
  H2/2/H2O/5/CO/2/CO2/3/
!********************** CH3CO ******************************************
!****************************************************************************
CH2HCO+H=CH3CO+H                3.000E+13  0.00    0.0
CH2HCO=CH3CO                    1.000E+16  0.00    22143.4
CH3CO(+M)=CH3+CO(+M)            2.800E+12  0.00    8550.0
  H2/2/H2O/5/CO/2/CO2/3/
  TROE /5.000E-01  1.000E-30  1.000E+30 /
  LOW /2.100E+14   .000    7000./
CH3CO+OH=CH2CO+H2O              1.200E+13  0.00    0.0
CH3CO+O=CH2CO+OH                4.000E+13  0.00    0.0
CH3CO+O=CH3+CO2                 1.500E+14  0.00    0.0
CH3CO+H=CH2CO+H2                2.400E+14  0.00    0.0
CH3CO+H=CH3+HCO                 2.100E+13  0.00    0.0
!********************** C2H4 ******************************************
!****************************************************************************
C2H4+OH=CH2O+CH3                7.000E+12  0.00    2990.0
CH3O+C2H3=CH2O+C2H4             2.410E+13  0.00    0.0
CH2OH+C2H3=CH2O+C2H4            4.200E+13  0.00    0.0
CH2OH+CH2=C2H4+OH               2.400E+13  0.00    0.0
CH3OH+C2H3=CH3O+C2H4            1.440E+01  3.10    3450.0
CH3OH+C2H3=CH2OH+C2H4           3.190E+01  3.20    3600.0
C2H4+OH=C2H3+H2O                2.300E+05  2.53    1115.0
C2H4+OH=C2H3OH+H                6.200E+12  0.00    2900.0
C2H4+OH=CH3CHO+H                6.200E+12  0.00    2900.0
C2H4+H=C2H3+H2                  6.000E+02  3.63    5670.0
C2H4+O2=C2H3+HO2                4.200E+13  0.00    28800.0
C2H4+O2=CH2HCO+OH               2.000E+08  1.50    18500.0
C2H3+HCO=C2H4+CO                2.500E+13  0.00    0.0
C2H3+H2O2=C2H4+HO2              1.210E+10  0.00    -297.0
C2H3+CH2O=C2H4+HCO              5.420E+03  2.81    2931.0
2C2H3=C2H2+C2H4                 1.500E+13  0.00    0.0
CH2HCO+CH2=C2H4+HCO             5.000E+13  0.00    0.0
CH2+CH3=C2H4+H                  4.220E+13  0.00    0.0
C2H4+M=C2H3+H+M                 7.400E+17  0.00    48603.6
  CH4/3/C2H6/3/O2/0.4/H2O/6.5/CO/0.75/CO2/1.5/AR/0.2/
C2H4+M=C2H2+H2+M                9.970E+16  0.00    36001.9
  CH4/3/C2H6/3/O2/0.4/H2O/6.5/CO/0.75/CO2/1.5/AR/0.35/
```

```
C2H4+O=CH2CO+H2                 6.800E+05  1.88    90.2
C2H4+O=CH3+HCO                  8.130E+06  1.88    90.2
C2H4+O=H+CH2HCO                 4.740E+06  1.88    90.2
C2H4+CH3=CH4+C2H3               6.000E+07  1.56    8370.0
CH4+CH=C2H4+H                   3.010E+13  0.00    -199.7
!********************** CH3CHO ****************************************
!**************************************************************************
CH3CHO(+M)<=>CH3+HCO(+M)      2.450E+022  -1.740  43460.0
  LOW/1.030E+059   -11.300   48270.0/
  TROE/2.490E-003  7.181E+002  6.089E+000  3.780E+003/
CH3CHO(+M)<=>CH4+CO(+M)       2.720E+021  -1.740  43460.0
  LOW/1.144E+058   -11.300   48270.0/
  TROE/2.490E-003  7.181E+002  6.089E+000  3.780E+003/
CH3CHO+O2=CH3CO+HO2             3.000E+13  0.00    19500.0
CH3CHO+HO2=CH2HCO+H2O2          2.320E+11  0.40    7498.7
CH3CHO+HO2=H2O2+CH3CO           3.010E+12  0.00    6000.0
CH3CHO+CH3=CH2HCO+CH4           2.450E+01  3.15    2883.7
CH3CHO+CH3=CH4+CH3CO            0.410E-06  5.60    1230.0
CH3CHO+H=CH2HCO+H2              2.100E+09  1.16    1210.0
CH3CHO+H=H2+CH3CO               2.100E+09  1.16    1210.0
CH3CHO+O=CH2HCO+OH              2.900E+12  0.00    900.0
CH3CHO+O=CH3CO+OH               2.900E+12  0.00    900.0
CH3CHO+OH=CH2HCO+H2O            2.700E+08  1.35    -729
CH3CHO+OH=CH3CO+H2O             3.000E+08  1.35    -729
!********************** C2H5 ******************************************
!**************************************************************************
CH4+CH3=C2H5+H2                 1.020E+13  0.00    11601.0
CH2OH+C2H5=CH3OH+C2H4           2.400E+12  0.00    0.0
CH2HCO+CH3=C2H5+HCO             1.000E+14  0.00    0.0
C2H5+O=CH2O+CH3                 6.620E+13  0.00    0.0
2CH3=C2H5+H                     6.010E+13  0.00    6480.0
O2+C2H5=C2H4+HO2                1.020E+10  0.00    -1100.5
C2H4+H(+M)=C2H5(+M)             3.970E+09  1.28    649.5
  CH4/3/C2H6/3/O2/0.4/H2O/6.5/CO/0.75/CO2/1.5/AR/0.35/
  TROE /7.600E-01  4.000E+01  1.025E+03 /
  LOW /1.350E+19   .000     380./
!********************** C2H6 ******************************************
!**************************************************************************
CH3O+C2H5=CH2O+C2H6             2.410E+13  0.00    0.0
CH2OH+C2H5=CH2O+C2H6            2.400E+12  0.00    0.0
C2H+C2H6=C2H2+C2H5              4.060E+12  0.28    -62.0
CH4+CH3=C2H6+H                  4.000E+14  0.00    20086.0
C2H6+C2H3=C2H4+C2H5             1.500E+13  0.00    5000.0
C2H6+CH2=CH3+C2H5               6.500E+12  0.00    3855.0
C2H6+O2=C2H5+HO2                6.000E+13  0.00    25500.0
2CH3(+M)=C2H6(+M)               4.500E+13  0.00    0.0
  H2/2/CH4/2/C2H6/3/O2/0.4/H2O/6/CO/1.5/CO2/2/AR/0.7/
  TROE /6.200E-01  7.300E+01  1.180E+03 /
  LOW  /1.200E+41 -7.000    1380./
C2H6+HO2=H2O2+C2H5              1.320E+13  0.00    10299.5
C2H6+OH=C2H5+H2O                7.230E+06  2.00    435.4
C2H6+O=C2H5+OH                  1.000E+09  1.50    2920.4
C2H6+CH3=C2H5+CH4               1.510E-07  6.00    3043.1
C2H6+CH2(S)=CH3+C2H5            2.400E+14  0.00    0.0
C2H6+CH=C2H4+CH3                1.080E+14  0.00    -132.3
C2H6+H=C2H5+H2                  1.450E+09  1.50    3729.8
!********************** C2H5O2 ****************************************
!**************************************************************************
C2H5+O2(+M)=C2H5O2(+M)          2.000E+11  0.98    -31.5
```

```
  TROE /0.103E-01  6.010E+02  1.000E+30  1.000E+30/
  LOW /1.50E+06  -4.29   110.0/
C2H5O2(+M)= C2H4+HO2(+M)       7.140E+04  2.32    14000.0
  TROE /0.000E-00  1.060E+02  1.000E+30  1.000E+30/
  LOW /8.30E+21  -0.651   11445.0/
C2H5O2=CH2CH2O2H                  7.940E+06  1.79    17900.0
C2H5O2= CH3CHO+OH                 1.320E+09  1.37    20790.0
C2H5O2= CH3CH2O+O                 2.980E+15  -0.09   30800.0
CH2CH2O2H= C2H4+HO2               1.280E+11  0.52    8075.0
C2H5O2+C2H5O2=CH3CH2O+CH3CH2O+O2  3.230E+10  0.00    124.0
C2H5O2+C2H5O2=CH3CHO+C2H5OH+O2    1.640E+10  0.00    124.0
C2H5O2+HO2=C2H5O2H+O2             1.620E+10  0.00    -994.0
!********************** CH2CH2OH ***************************************
!***************************************************************************
C2H4+OH=CH2CH2OH               1.260E+36  -7.752  3473.1
CH3CHOH=CH2CH2OH               5.820E+44  -10.34  27648.0
CH2CH2OH+O2=O2C2H4OH           0.500E+12  0.00    0.0
CH2CH2OH+O2=C2H3OH+HO2         0.500E+12  0.00    0.0
CH2CH2OH+O2=2CH2O+OH           4.000E+12  0.00    0.0
O2C2H4OH=C2H3OH+HO2            2.820E+08  1.361   15000.6
!********************** CH3CH2O ****************************************
!***************************************************************************
CH3CH2O+OH=CH3CHO+H2O          1.000E+13  0.00    0.0
CH3CH2O+H=C2H4+H2O             3.000E+13  0.00    0.0
CH3CH2O+H=CH3+CH2OH            3.000E+13  0.00    0.0
CH3CH2O+CO=C2H5+CO2            4.680E+02  3.20    2707.6
CH3CH2O+O2=CH3CHO+HO2          4.000E+10  0.00    553.6
CH3CH2O+M=CH3+CH2O+M           1.350E+38  -6.96   11900.8
CH3CH2O+M=CH3CHO+H+M           1.160E+35  -5.89   12637.8
C2H5+HO2=CH3CH2O+OH            4.000E+13  0.00    0.0
!********************** CH3CHOH ****************************************
!***************************************************************************
*
CH3CHOH+M=CH3CHO+H+M           1.000E+14  0.00    12581.8
  H2/2/CH4/2/H2O/6/CO/1.5/CO2/2/AR/0.7/
CH3CHOH+OH=CH3CHO+H2O          5.000E+12  0.00    0.0
CH3CHOH+HO2=CH3CHO+2OH         4.000E+13  0.00    0.0
CH3CHOH+H=CH3+CH2OH            3.000E+13  0.00    0.0
CH3CHOH+H=C2H4+H2O             3.000E+13  0.00    0.0
CH3CHOH+O=CH3CHO+OH            1.000E+14  0.00    0.0
CH3CHOH+O2=CH3CHO+HO2          5.280E+17  -1.64   419.5
CH3CHOH+O2=C2H3OH+HO2          7.620E+02  2.45    -148.5
CH3CHOH+O2=C2H4O2OH            4.05E+13   -0.31   -118.0
C2H4O2OH=C2H3OH+HO2            2.82E+08   1.361   15000.0
CH3CHOH=CH3CH2O                1.810E+55  -13.31  26600.0
!********************** C2H3OH  ****************************************
!***************************************************************************
C2H3OH+O2<=>CH2HCO+HO2         5.310E+11  0.210   1.983E+04
C2H3OH+H<=>CH2HCO+H2           9.810E+02  3.370   1.737E+03
C2H3OH+O<=>CH2HCO+OH           1.875E+06  1.900   -4.300E+02
C2H3OH+OH<=>CH2HCO+H2O         3.330E+09  1.100   2.705E+02
C2H3OH+CH3<=>CH2HCO+CH4        2.030E-08  5.900   0.552E+03
C2H3OH+HO2<=>CH3CHO+HO2        1.490E+05  1.670   3405.0
C2H4O2OH=CH3CHO+HO2            8.940E+31  -6.81   8000.0
C2H3OH+CH3O2<=>CH2HCO+CH3O2H   3.400E+03  2.500   4.992E+03
!********************** C2H5O2H ****************************************
!***************************************************************************
C2H5O2H=CH3CH2O+OH                2.500E+13  0.00    18800.0
C2H5O2+CH4=C2H5O2H+CH3            6.030E+12  0.00    19380.0
```

```
C2H5O2+C2H6=C2H5O2H+C2H5          6.030E+12  0.00    19380.0
C2H5O2+C2H5OH=C2H5O2H+CH2CH2OH    6.030E+12  0.00    19380.0
!********************* C2H5OH ******************************************
!***************************************************************************
!!!!!!!!!!!!!!!!!!!!!!!!H-Abstaction!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
C2H5OH+O=CH3CHOH+OH             1.450E+05  2.470   441.0
C2H5OH+O=CH2CH2OH+OH            9.690E+02  3.230   2344.0
C2H5OH+O=CH3CH2O+OH             1.460E-03  4.730   869.0
C2H5OH+H=CH3CHOH+H2             5.000E+04  2.680   1467.0
C2H5OH+H=CH2CH2OH+H2            8.000E+04  2.810   3772.0
C2H5OH+H=CH3CH2O+H2             9.450E+02  3.140   4379.0
C2H5OH+OH=CH3CHOH+H2O           7.160E+04  2.54    -772
C2H5OH+OH=CH2CH2OH+H2O          5.700E+00  3.380   -1205
C2H5OH+OH=CH3CH2O+H2O           5.810E-03  4.280   -1792
C2H5OH+HO2=CH3CHOH+H2O2         8.200E+03  2.50    5435.3
C2H5OH+HO2=CH2CH2OH+H2O2        2.430E+04  2.50    7951.7
C2H5OH+HO2=CH3CH2O+H2O2         3.800E+12  0.00    12078.5
C2H5OH+CH3=CH3CHOH+CH4          1.993E+01  3.370   3842.0
C2H5OH+CH3=CH2CH2OH+CH4         0.700E+02  3.300   6185.0
C2H5OH+CH3=CH3CH2O+CH4          2.035E+00  3.570   3886.0
C2H5OH+CH3O=CH3CHOH+CH3OH       1.220E-05  5.26    3737.5
C2H5OH+CH3O=CH2CH2OH+CH3OH      1.990E-02  4.30    7667.5
C2H5OH+CH3O=CH3CH2O+CH3OH       3.230E-07  5.30    5238.1
!!!!!!!!!!!!!!!!!!!!!!!!!!!!Decomposition!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
C2H5OH(+M)=C2H5+OH(+M)          6.170E+51  -10.30  55330.7
  H2/2/H2O/5/CO/2/CO2/3/
  TROE /5.000E-01  1.000E+30  1.000E+30 /
  LOW /8.100E+046   -11.300    55890.4/
C2H5OH(+M)=C2H4+H2O(+M)         8.000E+13  0.00    32680.6
  H2/2/H2O/6/CO/1.5/CO2/2/CH4/2/AR/0.7/HE/0.7/
  TROE /5.000E-01  1.000E+30  1.000E+30 /
  LOW /1.000E+17  00.000   27147./
C2H5OH(+M)=CH3+CH2OH(+M)        5.000E+15  0.00    41231.6
  H2/2/H2O/6/CO/1.5/CO2/2/CH4/2/AR/0.7/HE/0.7/
  TROE /5.000E-01  1.000E+30  1.000E+30 /
  LOW /3.000E+16  00.000   29155.6/
C2H5OH(+M)=CH3CHO+H2(+M)        2.470E+13  0.00    43370.6
  H2/2/H2O/6/CO/1.5/CO2/2/CH4/2/AR/0.7/HE/0.7/
  TROE /5.000E-01  1.000E+30  1.000E+30 /
  LOW /1.820E+41  -13.08   33790.6/
!********************* C3H2 ********************************************
!***************************************************************************
C3H2+OH=C2H2+CO+H             5.000E+13  0.00    0.0
C3H2+O=C2H+H+CO               6.800E+13  0.00    0.0
C3H2+O2=C2H2+CO2              2.000E+12  0.00    0.0
O2+C3H2=HCO+HCCO              1.000E+13  0.00    0.0
!********************* H2CCCH ******************************************
!***************************************************************************
H2CCCH+OH=HCO+C2H3            4.00E+13   0.00    0.0
H2CCCH+H=C3H2+H2              5.00E+12   0.00    0.0
H2CCCH+O=CH2O+C2H             1.40E+14   0.00    0.0
H2CCCH+O2=CO+CH3CO            3.01E+10   0.00    1443.0
H2CCCH+O2=CO2+C2H3            3.01E+10   0.00    1443.0
2C2H3=H2CCCH+CH3              1.80E+13   0.00    0.0
C2H2+HCCO=CO+H2CCCH           1.00E+11   0.00    1500.0
C2H2+CH2=H2CCCH+H             1.20E+13   0.00    3310.0
CH3+C2H=H2CCCH+H              2.41E+13   0.00    0.0
H2CCCH+OH=C3H2+H2O            2.00E+13   0.00    0.0
H2CCCH+O=C2H2+CO+H            1.39E+14   0.00    0.0
```

```
O2+H2CCCH=CH2CO+HCO          3.01E+10   0.00    1443.3
C2H2+CH2(S)=H2CCCH+H         1.75E+14   0.00    0.0
!********************** C3H4 *********************************************
!*****************************************************************************
C3H4+C2H5=H2CCCH+C2H6        2.20E+00   3.50    3300.0
C3H4+C2H3=H2CCCH+C2H4        2.20E+00   3.50    2350.0
C3H4+C2H=H2CCCH+C2H2         1.00E+13   0.00    0.0
C3H4+CH3=H2CCCH+CH4          1.80E+12   0.00    3850.0
C3H4+OH=H2CCCH+H2O           3.10E+06   2.00    50.0
C3H4+OH=CH2CO+CH3            4.30E+11   0.00    -400.0
C3H4+H=H2CCCH+H2             5.10E+05   2.50    1250.0
C3H4+HO2=H2CCCH+H2O2         9.60E+03   2.60    6800.0
C3H4+H=CH3+C2H2              2.00E+13   0.00    1200.0
C3H4+O=CO+C2H4               7.80E+12   0.00    800.0
C3H4+O=C2H3+HCO              1.10E-02   4.60   -2122.0
C3H4+O=OH+H2CCCH             6.00E+10   0.70   3800.0
C3H4+O=HCCO+CH3              7.30E+12   0.00   1000.0
C3H4+O2=H2CCCH+HO2           6.00E+13   0.00   25500.0
H2CCCH+H(+M)=C3H4(+M)        3.00E+13   0.00   0.0
  TROE /5.000E-01  1.000E+30  1.00E+30 /
  LOW /9.000E+15   1.000       0./
C2H4+CH=C3H4+H               1.320E+14  0.00    -173.2
C2H2+CH2=C3H4                1.200E+13  0.00    3330.5
!********************** C3H5 *********************************************
!*****************************************************************************
C3H5+C2H5=C3H4+C2H6          9.64E+11   0.00    -66.2
C3H5+C2H3=C3H4+C2H4          2.41E+12   0.00    0.0
C3H5+HO2=>C2H3+CH2O+OH       6.25E+12   0.00    0.0
C3H5+HO2=OH+HCO+C2H4         5.00E+12   0.00    0.0
C3H5+OH=C3H4+H2O             6.02E+12   0.00    0.0
C3H5+OH=CH2O+C2H4            1.50E+13   0.00    0.0
C3H5+H=C3H4+H2               1.80E+13   0.00    0.0
CH3+C2H3=C3H5+H              1.50E+24   -2.83   9369.9
C3H5+O=>C2H4+CO+H            1.81E+14   0.00    0.0
C3H5+O=CH2CO+CH3             1.80E+14   0.00    0.0
C3H5+O2=C3H4+HO2             1.00E+12   0.00    11400.0
C3H5+O2=CO+CH2O+CH3          4.30E+12   0.00    9450.0
C3H4+H(+M)=C3H5(+M)          4.00E+13   0.00    0.0
  TROE /8.000E-01  1.000E+15  1.000E+30 /
  LOW /3.000E+24  -2.000       0./
C2H2+CH3=C3H5                2.300E+30  -5.98   6710.4
C2H3+C2H5=C3H5+CH3           3.900E+32  -5.22   9857.0
!********************** C3H6 *********************************************
!*****************************************************************************
C3H6+C2H5=C3H5+C2H6          1.00E+11   0.00    4940.0
C3H6+C2H3=C3H5+C2H4          3.02E+12   0.00    7310.0
C3H6+C2H=C3H4+C2H3           1.20E+13   0.00    0.0
C3H6+CH2=C3H5+CH3            7.00E+11   0.00    3100.0
C3H6+CH3=C3H5+CH4            2.21E+00   3.50    2859.0
C3H6+HO2=C3H5+H2O2           9.64E+03   2.60    7003.0
C3H6+OH=C2H5+CH2O            1.00E+12   0.00    0.0
C3H6+OH=C3H5+H2O             3.12E+06   2.00    -151.0
C3H6+H=C2H4+CH3              8.00E+21   -2.39   5540.0
C3H6+H=C3H5+H2               6.46E+12   0.00    2223.0
C3H6+O=C2H4+CH2O             6.76E+04   2.56    -570.0
C3H6+O=C2H5+HCO              6.76E+04   2.56    -570.0
C3H6+O=C3H5+OH               1.80E+11   0.70    2959.2
C3H6+O=CH2CO+CH3+H           1.20E+08   1.65    164.6
C3H6+O=CH3+CH3CO             9.11E+06   1.60    -314.0
```

```
C3H6+O2=C3H5+HO2              1.08E+03   2.50    17980.0
C3H6=C2H2+CH4                 3.50E+12   0.00    35000.0
C3H6=C3H4+H2                  4.00E+13   0.00    40000.0
C3H5+H(+M)=C3H6(+M)           1.67E+14   0.00    0.0
  H2/2/CH4/2/C2H6/3/H2O/6/CO/1.5/CO2/2/AR/0.7/
  TROE /2.000E-02  1.097E+03  1.097E+03  6.860E+03 /
  LOW /1.330E+60  -12.000    3003./
CH3+C2H3(+M)=C3H6(+M)         2.500E+13  0.00    0.0
  H2/2/CH4/2/C2H6/3/H2O/6/CO/1.5/CO2/2/AR/0.7/
  TROE /1.750E-01  1.341E+03  6.000E+04  1.014E+04 /
  LOW /4.270E+58  -11.940    4917./
C3H5+C2H3=C3H6+C2H2           4.80E+12   0.00    0.0
C3H5+CH2O=C3H6+HCO            7.20E+07   1.80    9155.0
2C3H5=C3H4+C3H6               8.43E+10   0.00    -132.0
C3H5+C3H4=H2CCCH+C3H6         1.00E+12   0.00    3850.0
C3H5+C2H5=C2H4+C3H6           2.60E+12   0.00    -66.0
C2H4+CH2=C3H6                 6.60E+12   0.00     0.0
C2H4+CH2(S)=C3H6              9.64E+13   0.00     0.0
!************************ nC3H7 ***************************************
!**********************************************************************
C3H6+H(+M)=nC3H7(+M)         1.330E+13   0.00    1641.0
   H2/2/CH4/2/C2H6/3/H2O/6/CO/1.5/CO2/2/AR/0.7/
   TROE /1.000E+00  1.000E+03  1.310E+03  4.810E+04 /
   LOW /6.260E+38  -6.660    3523./
nC3H7+O2=C3H6+HO2             9.000E+10  0.00    0.0
nC3H7=C2H4+CH3                1.260E+13  0.00    15000.0
!*********************************iC3H7***************************************
!**********************************************************************
iC3H7+CH3=CH4+C3H6            2.20E+14   -0.68   0.0
C3H6+H(+M)=iC3H7(+M)          1.33E+13   0.00    785.0
   H2/2/ CH4/2/ C2H6/3/ H2O/6/ CO/1.5/ CO2/2/ AR/0.7/
   TROE /1.000E+00  1.000E+03  6.454E+02  6.844E+03 /
   LOW /8.700E+42  -7.500    2376./
iC3H7+O2=C3H6+HO2             1.30E+11   0.00    0.0
!********************** C3H8 ***************************************
!**********************************************************************
iC3H7+H = C3H8                1.66E+13   0.2200  0.00
2iC3H7=C3H6+C3H8              2.40E+12   0.00    0.0
C3H8+iC3H7=nC3H7+C3H8         8.40E-03   4.20    4366.1
C3H8+C3H5=iC3H7+C3H6          2.00E+11   0.00    8140.0
C3H8+C3H5=nC3H7+C3H6          7.94E+11   0.00    10400.0
C3H8+O2=iC3H7+HO2             3.98E+13   0.00    24000.0
C3H8+O2=nC3H7+HO2             3.98E+13   0.00    24000.0
C3H8+CH3=iC3H7+CH4            1.10E+15   0.00    12700.0
C3H8+CH3=nC3H7+CH4            1.10E+15   0.00    12700.0
C3H8+HO2=iC3H7+H2O2           9.64E+03   2.60    6955.0
C3H8+HO2=nC3H7+H2O2           1.12E+13   0.00    9810.0
C3H8+OH=iC3H7+H2O             4.79E+08   1.40    430.0
C3H8+OH=nC3H7+H2O             5.75E+08   1.40    430.0
C3H8+O=iC3H7+OH               4.76E+04   2.71    1058.5
C3H8+O=nC3H7+OH               1.90E+04   2.68    2117.0
C3H8+H=iC3H7+H2               1.30E+06   2.40    2249.2
C3H8+H=nC3H7+H2               1.33E+06   2.54    3403.0
C3H8=nC3H7+H                  1.58E+16   0.00    49074.0
C3H8(+M)=CH3+C2H5(+M)         1.10E+17   0.00    42459.0
   H2/2.5/ H2O/12/CO/1.9/CO2/3.8/AR/0.75/HE/0.75/
   TROE /5.000E-01  1.000E+15  1.000E+30 /
   LOW /7.830E+18   .000   32716./
C3H8+C2H5O2=iC3H7+C2H5O2H     1.990E+12   0.00    17050.0
```

```
C3H8+C2H5O2=nC3H7+C2H5O2H   6.030E+12   0.00    19380.0
!************************ C4H2 ****************************************
!**********************************************************************
C4H2+OH=C3H2+HCO             0.40E+13   0.00    000.0
C4H2+OH = C4H+H2O            4.00E+12   0.000   0.0
C4H2+O=C3H2+CO               7.89E+12   0.00    678.4
C2H2+C2H=C4H2+H              5.00E+12   0.00    0.0
C4H2+M=C4H+H+M               3.50E+17   0.0     40293.0
DUPLICATE
C4H2=  2C2H                  1.00E+16   0.00    73000.0
!************************ H2CCCCH *************************************
!**********************************************************************
H2CCCCH+C2H3=2H2CCCH         4.00E+12   0.00    0.0
H2CCCCH+CH2=C3H4+C2H         2.00E+13   0.00    0.0
H2CCCCH+H2=C2H2+C2H3         5.01E+10   0.00    10000.0
H2CCCCH+O2=CH2CO+HCCO        3.92E+16   -1.8    -1.200
H2CCCCH+OH=C4H2+H2O          4.00E+12   0.00    0.0
H2CCCCH+O=CH2CO+C2H          2.00E+13   0.00    0.0
H2CCCCH+H=C4H2+H2            5.00E+12   0.00    0.0
C3H2+CH2=H2CCCCH+H           3.00E+13   0.00    0.0
C2H2+C2H=H2CCCCH             7.00+13    0.00    0.00
H2CCCH+CH=H2CCCCH+H          7.00E+13   0.00    23408.7
2C2H2=H2CCCCH+H              1.10E+14   0.00    33202.0
C4H2+H(+M)=H2CCCCH(+M)       4.30E+10   1.158   876.5
   TROE /9.000E-01  1.000E+15  1.000E+30 /
   LOW /3.830E+21  -8.095   1253.5/
!************************ C4H4 ****************************************
!**********************************************************************
C4H4+C2H3=H2CCCCH+C2H4       5.00E+11   0.00    8150.0
C4H4+C2H=H2CCCCH+C2H2        4.00E+13   0.00    0.0
C4H4+C2H=C4H2+C2H3           1.00E+13   0.00    0.0
C4H4+OH=H2CCCCH+H2O          7.50E+06   2.00    2525.9
C4H4+O=C3H4+CO               6.00E+13   0.00    920.0
C2H3+C2H2=H+C4H4             2.00E+11   0.00    2500.0
H2CCCH+CH2=H+C4H4            4.00E+13   0.00    0.0
C4H4+H=H2CCCCH+H2            5.01E+06   2.00    3000.0
C4H4+O=HCO+H2CCCH            3.20E+08   1.44    276.5
C4H4+M=H2CCCCH+H+M           1.10E+20   0.00    49638.8
!H2CCCCH+H=C4H4              5.00E+14   0.00    405.0
C4H4=2C2H2                   1.15E+15   0.00    43541.0
C3H2+CH3=C4H4+H              1.00E+12   0.00    0.0
C2H4+C2H=C4H4+H              1.20E+13   0.00    0.0
!************************ i-C4H5 **************************************
!**********************************************************************
i-C4H5+C2H=2H2CCCH           4.00E+12   0.00    0.0
i-C4H5+OH=C4H4+H2O           2.00E+07   2.00    502.8
i-C4H5+H=H2CCCH+CH3          2.00E+13   0.00    1000.0
i-C4H5+H=C4H4+H2             1.00E+14   0.00    0.0
i-C4H5+O2=CH2CO+CH2HCO       7.50E+15   -1.37   5993.5
i-C4H5+O2=C4H4+HO2           7.50E+11   0.21    7143.4
i-C4H5(+M)=C4H4+H(+M)        1.00E+14   0.00    25001.2
  LOW /2.000E+15   .000   21000./
i-C4H5+M=C2H3+C2H2+M         1.000E+15  0.70    21290.0
2C2H3=i-C4H5+H               4.000E+13  0.00    0.0
!************************ C4H6 ****************************************
!**********************************************************************
C4H6+H2CCCH=i-C4H5+C3H4      1.00E+13   0.00    9830.0
C4H6+C2H3=i-C4H5+C2H4        5.00E+14   0.00    9980.0
C4H6+CH3=i-C4H5+CH4          7.00E+13   0.00    7810.0
```

```
C4H6+OH=CH3CHO+C2H3          2.80E+12   0.00    -400.0
C4H6+OH=C2H5+CH2CO           1.00E+12   0.00    0.0
C4H6+OH=i-C4H5+H2O           3.10E+06   2.00    202.0
C4H6+H=i-C4H5+H2             6.60E+05   2.53    4636.5
C4H6+H=C3H4+CH3              2.50E+13   0.00    1042.0
C4H6+O=C3H5+CO+H             6.00E+08   1.45    440.0
C4H6+O=i-C4H5+OH             7.11E+08   1.55    2345.5
C4H6+O2=i-C4H5+HO2           4.00E+13   0.00    28400.0
C4H6=C2H2+C2H4               1.00E+14   0.00    37000.0
C4H6=C4H4+H2                 2.50E+15   0.00    47000.0
C4H6 = i-C4H5 + H            5.70E+36   -6.27   56176.5
H2CCCH+CH3(+M) = C4H6(+M)    1.50E+12    0.0    0.0
   LOW /2.60E+57 -11.94     4885.9 /
   TROE /0.175 1340.6 60000.0 9769.8  /
   H2/2.0/H2O/6.0/CH4/2.0/CO/1.5/CO2/2.0/C2H6/3.0/AR/0.7/
C2H4+C2H3=C4H6+H             5.00E+11   0.00    3680.0
2C2H3=C4H6                   4.94E+13   0.00    0.0
!*************************** nC4H7 ****************************************
!**************************************************************************
nC4H7+C3H5=C4H6+C3H6         1.40E+12   0.00    0.0
nC4H7+C2H5=C4H6+C2H6         3.98E+12   0.00    0.0
nC4H7+C2H3=C4H6+C2H4         3.98E+12   0.00    0.0
nC4H7+CH3=C4H6+CH4           1.00E+13   0.00    0.0
nC4H7+H=C4H6+H2              3.16E+13   0.00    0.0
nC4H7+O2=C4H6+HO2            1.00E+11   0.00    0.0
nC4H7+M=C3H4+CH3+M           1.00E+13   0.00    16300.0
nC4H7+M=C2H4+C2H3+M          1.00E+11   0.00    18600.0
nC4H7+M=C4H6+H+M             1.20E+14   0.00    24800.0
!*************************** C4H8 *****************************************
!**************************************************************************
nC4H7+C2H5=C4H8+C2H4         5.01E+11   0.00    0.0
C4H8=nC4H7+H                 1.26E+15   0.00    41496.3
C4H8=C3H5+CH3                1.00E+16   0.00    36685.3
C2H3+C2H5=>C4H8              9.00E+12   0.00    0.0
C4H8+C3H5=nC4H7+C3H6         8.00E+10   0.00    6522.3
C4H8+H=nC4H7+H2              2.00E+14   0.00    1900.0
C4H8+HO2=nC4H7+H2O2          3.00E+11   0.00    8500.0
C4H8+C2H5=nC4H7+C2H6         4.00E+11   0.00    4025.7
C4H8+CH3=nC4H7+CH4           2.00E+12   0.00    4400.0
C4H8+OH=nC4H7+H2O            1.00E+13   0.00    600.0
C4H8+O=nC4H7+OH              1.00E+05   2.56    -550.0
C4H8+OH=CH2O+nC3H7           3.00E+12   0.00    0.0
C4H8+OH=CH3CHO+C2H5          2.00E+11   0.00    0.0
C4H8+O=CH3CHO+C2H4           1.00E+12   0.00    0.0
C4H8+O=>C2H5+CH3+CO          2.60E+13   0.00    40.0
C4H8+O=C3H6+CH2O             2.00E+12   0.00    0.0
C4H8+OH=>C2H6+CH3+CO         4.00E+10   0.00    0.0
C4H8+O=nC3H7+HCO             1.00E+06   2.34    -500.0
!*************************** tC4H9 ****************************************
!**************************************************************************
tC4H9=C2H4+C2H5              4.50E+13   0.00    15000.0
tC4H9+O2=iC4H8+HO2           1.00E+12   0.00    2400.0
!*************************** iC4H8 ****************************************
!**************************************************************************
iC4H8+M=C3H5+CH3+M           4.00E+18   0.00    37000.0
iC4H8+M=iC4H7+H+M            2.00E+17   0.00    43000.0
iC4H8+H=iC4H7+H2             2.00E+13   0.00    1900.0
iC4H8+O=iC4H7+OH             1.00E+05   2.56    -550.0
iC4H8+OH=iC4H7+H2O           1.00E+12   0.00    650.0
```

```
iC4H8+O=iC3H7+HCO            1.00E+06   2.34    -500.0
iC4H8+OH=iC3H7+CH2O          1.00E+12   0.00    0.0
iC4H8+CH3=iC4H7+CH4          1.00E+12   0.00    4400.0
iC4H8=C2H3+C2H5              2.00E+18  -1.00    48000.0
iC4H8+C2H5=iC4H7+C2H6        2.00E+11   0.00    4025.7
iC4H8+O2=iC4H7+HO2           4.00E+12   0.00    20000.0
iC4H8+OH=C2H6+CH3+CO         2.00E+10   0.00    0.0
iC4H8+O=C3H6+CH2O            2.00E+12   0.00    0.0
iC4H8+O=C2H5+CH3+CO          2.60E+13   0.00    40.0
iC4H8+HO2=iC4H7+H2O2         2.00E+11   0.00    8500.0
iC4H8=C4H6+H2                3.00E+15   0.00    32500.0
iC4H8+O=CH3CHO+C2H4          1.00E+12   0.00    0.0
iC4H8+OH=CH3CHO+C2H5         1.00E+11   0.00    0.0
iC4H7+C2H5=iC4H8+C2H4        5.01E+11   0.00    0.0
iC4H7+iC4H7=C4H6+iC4H8       3.16E+12   0.00    0.0
!************************ iC4H7 ***************************************
!**********************************************************************
iC4H7+M=C3H4+CH3+M           2.00E+13   0.00    16300.0
iC4H7+M=C4H6+H+M             1.20E+14   0.00    24800.0
iC4H7+M=C2H4+C2H3+M          1.00E+11   0.00    18600.0
iC4H7+O2=C4H6+HO2            1.00E+11   0.00    0.0
iC4H7+H=C4H6+H2              3.16E+13   0.00    0.0
iC4H7+C2H3=C4H6+C2H4         3.98E+12   0.00    0.0
iC4H7+C2H5=C4H6+C2H6         3.98E+12   0.00    0.0
iC4H7+CH3=C4H6+CH4           1.00E+13   0.00    0.0
iC4H7+C3H5=C4H6+C3H6         1.40E+12   0.00    0.0
!***************************** nC4H9 ***********************************
!**********************************************************************
C4H8+H=>nC4H9                2.501E+11  0.51    1318.0
nC4H9=CH3+C3H6               2.300E+14  0.00    16500.0
nC4H9+O2=C4H8+HO2            2.000E+12  0.00    2400.0
nC4H9=C2H4+C2H5              9.000E+13  0.00    15000.0
!***************************** sC4H9 ***********************************
!**********************************************************************
C4H8+H=>sC4H9                2.501E+11  0.51    1318.0
sC4H9=CH3+C3H6               2.300E+14  0.00    16500.0
sC4H9+O2=C4H8+HO2            2.000E+12  0.00    2400.0
sC4H9=C2H4+C2H5              9.000E+13  0.00    15000.0
!***************************** nC4H10 **********************************
!**********************************************************************
nC4H10+CH3O=sC4H9+CH3OH      6.000E+11  0.00    3500.0
nC4H10+CH3O=nC4H9+CH3OH      3.000E+11  0.00    3500.0
nC4H10+C3H5=sC4H9+C3H6       3.162E+11  0.00    8200.0
nC4H10+C3H5=nC4H9+C3H6       7.943E+11  0.00    10250.0
nC4H10+C2H5=sC4H9+C2H6       1.000E+11  0.00    5200.0
nC4H10+C2H5=nC4H9+C2H6       1.000E+11  0.00    6700.0
nC4H10+C2H3=sC4H9+C2H4       7.943E+11  0.00    8400.0
nC4H10+C2H3=nC4H9+C2H4       1.000E+12  0.00    9000.0
nC4H10+CH3=sC4H9+CH4         2.189E+11  0.00    4800.0
nC4H10+CH3=nC4H9+CH4         2.189E+11  0.00    5700.0
nC4H10+HO2=sC4H9+H2O2        4.000E+12  0.00    9750.0
nC4H10+HO2=nC4H9+H2O2        1.700E+13  0.00    10230.0
nC4H10+OH=sC4H9+H2O          7.234E+07  1.64    -123.0
nC4H10+OH=nC4H9+H2O          4.140E+07  1.73    376.5
nC4H10+O=sC4H9+OH            4.280E+05  2.60    1291.5
nC4H10+O=nC4H9+OH            4.890E+06  2.40    2752.5
nC4H10+H=sC4H9+H2            4.777E+06  2.50    3684.5
nC4H10+H=nC4H9+H2            5.630E+07  2.00    3850.0
nC4H10+O2=sC4H9+HO2          3.981E+13  0.00    42800.0
```

```
nC4H10+O2=nC4H9+HO2          2.512E+13  0.00    44500.0
nC4H10=sC4H9+H               1.000E+16  0.00    42500.0
nC4H10=nC4H9+H               1.580E+16  0.00    49000.0
nC4H10=iC3H7+CH3             1.000E+17  0.00    42700.0
nC4H10=nC3H7+CH3             1.000E+17  0.00    42700.0
nC4H10=C2H5+C2H5             2.000E+16  0.00    40650.0
!!!!!!!!!!!!!!!!!!!!!!!!!!LOW TEMPERATURE!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!********************** C4H9OO ****************************************
sC4H9+O2<=>C4H9OO            2.200E+19  -2.50   0.0
nC4H9+O2<=>C4H9OO            2.200E+19  -2.50   0.0
C4H9OO<=>C4H8OOH             3.000E+12  0.00    11050.0
C4H9OO=>OH+C3H6+CH2O         1.000E+12  0.00    11250.0
!************************ C4H8OOH ****************************************
C4H8OOH+O2=C4H8OOO2H         2.200E+19  -2.50   0.0
C4H8OOH=>OH+C3H6+CH2O        5.500E+12  0.00    8000.0
C4H8OOH<=>OH+C4H8O           8.000E+12  0.00    6250.0
C4H8OOH<=>HO2+C4H8           2.500E+12  0.00    8000.0
!************************ C4H8OOO2H **************************************
C4H8OOO2H=>OH+C4H8O3         5.000E+09  0.00    3750.0
!************************ C4H9OOH ****************************************
C4H9OOH=>OH+nC3H7+CH2O         7.00E+14   0.00    21000.0
C4H9OOH=>OH+C2H5+CH3CHO        7.00E+14   0.00    21000.0
C4H9OO+nC4H10=C4H9OOH+sC4H9    1.20E+01   3.49    6500.0
C4H9OO+nC4H10=C4H9OOH+nC4H9    2.40E+01   3.70    8000.0
!************************ C4H8O3 ****************************************
C4H8O3=>OH+HCO+C2H4+CH2O       7.00E+16   0.00    21000.0
C4H8O3=>CH3CHO+CH2HCO+OH       7.00E+16   0.00    21000.0
C4H8O3=>CH3+CH2HCO+HCO+OH      7.00E+16   0.00    21000.0
C4H8O3=>CH2O+C2H5+CO+OH        1.50E+16   0.00    21000.0
C4H8O3=>CH3CHO+CH3CO+OH        1.50E+16   0.00    21000.0
!************************ C4H8O ****************************************
nC3H7+HCO=C4H8O              5.21E+13   0.00    0.0
C4H =  C4+H                  2.00E+14   0.00    58000.0
C4H+H+M = C4H2 + M           3.00E+13   0.00    0.00
DUPLICATE
!********************** C5H8*****************************************
C5H8+OH=CH3CHO+C3H5          2.00E+12   0.00    0.0
!********************** C5H9*****************************************
C5H9+C3H5=C5H8+C3H6          4.00E+12   0.00    0.0
C5H9+O2=C5H8+HO2             2.10E+10   0.00    0.0
!********************** C5H9O****************************************
C5H9O=>2C2H4+HCO             2.90E+16   -1.21   13500.0
!********************** C5H10****************************************
C5H10+OH=C5H9+H2O            6.80E+13   0.00    1540.0
C5H10+O=>C3H6+C2H3+OH        1.00E+13   0.00    3520.0
C5H10+O=>C3H5+C2H4+OH        2.00E+13   0.00    3520.0
C5H10+O=nC3H7+CH2HCO         1.00E+12   0.00    0.0
C5H10+O=C5H9+OH              2.80E+14   0.00    430.0
C5H10+OH=nC3H7+CH3CHO        2.00E+12   0.00    0.0
C5H10+OH=nC4H9+CH2O          1.00E+12   0.00    0.0
C5H10+C2H5=C5H9+C2H6         1.70E+11   0.00    4000.0
C5H10+HO2=C5H9+H2O2          1.00E+11   0.00    8540.0
C5H10+OH=>C3H6+C2H3+H2O      1.00E+09   1.20    52.1
C5H10+OH=>C3H5+C2H4+H2O      2.00E+09   1.20    62.1
C5H10+O=C4H8+CH2O            2.00E+13   0.00    0.0
C5H10+O=C3H6+CH3CHO          1.00E+13   0.00    0.0
C5H10+H=C5H9+H2              2.80E+13   0.00    2010.0
!***************************** C5H11 ***********************************
C5H11+O2=C5H10+HO2           1.00E+12   0.00    2100.0
```

```
C5H11=C3H6+C2H5              1.01E+12   0.00    14800.0
C5H11=C4H8+CH3               8.00E+12   0.00    16000.0
C5H11=nC3H7+C2H4             3.20E+13   0.00    14300.0
!************************** iC5H11 ***************************************
iC5H11=iC3H7+C2H4            3.20E+13   0.00    14300.0
iC5H11=iC4H8+CH3             4.00E+12   0.00    16000.0
iC5H11=C5H10+H               3.90E+13   0.00    20400.0
iC5H11=C3H6+C2H5             1.01E+12   0.00    14800.0
iC5H11+O2=C5H10+HO2          1.00E+12   0.00    2100.0
!************************** iC4H9 ****************************************
iC4H9=iC4H8+H                1.00E+15   0.00    17000.0
iC4H9+O2=iC4H8+HO2           1.00E+12   0.00    2500.0
!*************************************************************************
!************************ aC6H12 ****************************************
aC6H12+OH=C5H11+CH2O         1.00E+11   0.00    0.0
aC6H12+OH=>C3H5+C3H6+H2O     6.50E+09   1.25    350.0
aC6H12+H=C3H5+C3H6+H2        1.00E+07   2.00    2500.0
aC6H12=2C3H6                 5.00E+13   0.00    28400.0
!************************** iC6H13 ***************************************
!*************************************************************************
iC6H13=aC6H12+H              2.00E+13   0.00    20000.0
iC6H13=C5H10+CH3             1.00E+10   0.00    13000.0
iC6H13=C3H6+iC3H7            1.00E+13   0.00    14000.0
iC6H13=tC4H9+C2H4            2.50E+13   0.00    15000.0
iC6H13+O2=aC6H12+HO2         2.00E+12   0.00    1000.0
iC6H13=iC4H8+C2H5            2.00E+12   0.00    11000.0
!************************** C6H13 ****************************************
!*************************************************************************
C6H13=C5H10+CH3              1.00E+10   1.08    14790.0
C6H13=aC6H12+H               1.00E+13   0.00    20000.0
C6H13=nC3H7+C3H6             6.00E+10   0.84    14001.0
C6H13=C4H8+C2H5              2.04E+13   0.04    14340.0
C6H13+O2=aC6H12+HO2          1.00E+12   0.00    2300.0
!************************** C6H12 ****************************************
!*************************************************************************
tC4H9+C2H2=C6H11             7.23E+10   0.00    4320.0
iC6H12+H=iC6H11+H2           1.00E+12   0.00    1950.0
iC6H12+OH=iC6H11+H2O         1.00E+11   0.00    615.0
iC6H12+O=iC6H11+OH           1.00E+12   0.00    2000.0
iC6H12+CH3=iC6H11+CH4        2.00E+11   0.00    3650.0
iC6H12=C2H3+iC4H9            2.50E+16   0.00    35000.0
iC6H12=iC3H7+C3H5            2.50E+16   0.00    35000.0
iC6H12=iC6H11+H              8.00E+17   0.00    50000.0
tC4H9+C2H2=iC6H11            7.23E+10   0.00    4320.0
iC6H11= C3H6+C3H5            4.50E+24  -3.00    2.25E+04
iC6H11=C5H8+CH3        4.50E+24  -3.00    2.25E+04
!************************** C6H11 ****************************************
!*************************************************************************
C6H11 = C2H5+C4H6      4.50E+23  -2.99    27000.0
C6H11 = C3H6 + C3H5    4.50E+24  -2.99    27000.0
C6H11 = C5H8 + CH3     4.50E+24  -2.99    27000.0
C4H8+C2H3=C6H11        7.23E+10   0.00    4320.00
!************************** C6H10 ****************************************
!*************************************************************************
C6H10 = C2H3+nC4H7     4.500E+23  -2.99   27000.0
C6H10 = C3H5 + C3H5    5.000E+22  -2.06   31185.0
C6H10 = C2H4+C4H6      1.000E+12   0.0    12100.0
END
```

```
!************************************************************************
!********************** CYCLO HEXANE ************************************
REACTIONS
!-------------------------------cy-Hexane decomposition---------------------
cyC6H12=cyC6H11+H             3.00E+16   0.00    95000.0    !(R1)[2]
cyC6H12=aC6H12                5.01E+16   0.00    88230.0    !(R2)[3]
cyC6H12=C3H6+C3H6             4.00E+12   0.0     57400.0    !(R3)[3]
cyC6H12=C4H8+C2H4             4.00E+12   0.0     57400.0    !(R4)[3]
cyC6H12=>C2H4+C2H4+C2H4       8.22E+17   0.00    87225.     !(R5)[4]
!-------------------------------atom abstraction---------------------------
cyC6H12+O2=cyC6H11+HO2        0.60E+13   0.00    50150.1    !(R6)[5]*0.5
cyC6H12+O=cyC6H11+OH          4.34E+09   1.33    3427.5     !(R7)!REAC_UQ
cyC6H12+H=cyC6H11+H2          2.70E+8    2.00    5000       !(R8)[6]
cyC6H12+OH=cyC6H11+H2O        1.3E+09    1.60    -400.5     !(R9)[7]
cyC6H12+HO2=cyC6H11+H2O2      0.44e+14   0.00    17690      !(R10)[5]*2
cyC6H12+HCO=cyC6H11+CH2O      1.35E+12   0.00    9540       !(R11)[2]
cyC6H12+CH3O=cyC6H11+CH3OH    4.32E+11   0.00    4473       !(R12)[2]
cyC6H12+CH3 =cyC6H11+CH4      1.35E+12   0.00    9540       !(R13)[4]
cyC6H12+C2H3=cyC6H11+C2H4     1.35E+12   0.00    9540       !(R14)[2]
cyC6H12+C2H5=cyC6H11+C2H6     1.35E+12   0.00    9540       !(R15)[2]
cyC6H12+C3H5=cyC6H11+C3H6     1.05E+12   0.00    9540       !(R16)[2]
!----------------------------cyC6H11 isomerization & decomposition----------
cyC6H11 = cyC6H10 + H         8.91E+11   0.834   36340      !(R17)[8]
cyC6H11 = C6H11               3.00e+12   0.624   30810      !(R18)[8]
!-------------------------cyC6H10 decomposition-----------------------------
cyC6H10 = cyC6H9 + H          1.20E+15   0.00    83200      !(R19)[9]
cyC6H10 = C6H10               5.00E+13   0.00    74000      !(R20)Anlg R2
cyC6H10 = C4H6+C2H4           4.00E+14   0.00    63400      !(R21)[4]*1.6
!----------------------------Dehydrogenation of cyC6H11--------------------
cyC6H11+O2=cyC6H10+HO2        1.17E+13   0.00    7479.7     !(R22)!EM
cyC6H11+O=cyC6H10+OH          1.31E+13   0.00    0.0        !(R23)!EM
cyC6H11+H=cyC6H10+H2          2.05E+13   0.00    0.0        !(R24)!EM
cyC6H11+OH=cyC6H10+H2O        1.28E+13   0.00    0.0        !(R25)!EM
cyC6H11+HO2=cyC6H10+H2O2      1.00E+12   0.00    2000.0     !(R26)[2]
cyC6H11+HCO=cyC6H10+CH2O      1.25E+13   0.00    0.0        !(R27)!EM
cyC6H11+CH3O=cyC6H10+CH3OH    1.25E+13   0.00    0.0        !(R28)!EM
cyC6H11+CH3 =cyC6H10+CH4      1.71E+13   0.00    0.0        !(R29)!EM
cyC6H11+C2H3=cyC6H10+C2H4     1.43E+13   0.00    0.0        !(R30)!EM
cyC6H11+C2H5=cyC6H10+C2H6     9.70E+12   0.00    0.0        !(R31)!EM
cyC6H11+C3H5=cyC6H10+C3H6     7.17E+12   0.00    0.0        !(R32)!EM
!-----------------------Dehydrogenation of cyC6H10-------------------------
cyC6H10+O2=cyC6H9+HO2         7.71E+12   0.00    38119      !(R33)!EM
cyC6H10+O=cyC6H9+OH           1.29E+13   0.00    6939.5     !(R34)!EM
cyC6H10+H=cyC6H9+H2           6.00E+12   0.00    4445       !(R35)[4]
cyC6H10+OH=cyC6H9+H2O         2.42E+13   0.00    2934.5     !(R36)!EM
cyC6H10+HO2=cyC6H9+H2O2       4.50E+10   0.60    15828      !(R37)!REAC_UQ
cyC6H10+HCO=cyC6H9+CH2O       6.17E+12   0.00    10602      !(R38)!EM
cyC6H10+CH3O=cyC6H9+CH3OH     1.23E+13   0.00    6628.7     !(R39)!EM
cyC6H10+CH3=cyC6H9+CH4        8.39E+12   0.00    6385       !(R40)!EM
cyC6H10+C2H3=cyC6H9+C2H4      7.07E+12   0.00    4827       !(R41)!EM
cyC6H10+C2H5=cyC6H9+C2H6      7.17E+12   0.00    7512       !(R42)!EM
cyC6H10+C3H5=cyC6H9+C3H6      1.42E+13   0.00    11059.5    !(R43)!EM
!-----------------------cyC6H9 decomposition-------------------------------
cyC6H9 = cyC6H8+ H            1.20E+14   0.00    49300.0    !(R44)![4]
!-----------------------Dehydrogenation cyC6H9-----------------------------
cyC6H9+O2=cyC6H8+HO2          6.43E+12   0.00    14237.5    !(R45)!EM
cyC6H9+O=cyC6H8+OH            8.58E+12   0.00    0.0        !(R46)!EM
cyC6H9+H=cyC6H8+H2            2.65E+13   0.00    0.0        !(R47)!EM
cyC6H9+OH=cyC6H8+H2O          8.08E+12   0.00    0.0        !(R48)!EM
```

```
cyC6H9+HO2=cyC6H8+H2O2       5.21E+12   0.00    2749.0    !(R49)!EM
cyC6H9+HCO=cyC6H8+CH2O       5.62E+12   0.00    2642.0    !(R50)!EM
cyC6H9+CH3O=cyC6H8+CH3OH     1.23E+13   0.00    0.0       !(R51)!EM
cyC6H9+CH3=cyC6H8+CH4        1.12E+13   0.00    0.0       !(R52)!EM
cyC6H9+C2H3=cyC6H8+C2H4      9.43E+12   0.00    0.0       !(R53)!EM
cyC6H9+C2H5=cyC6H8+C2H6      9.58E+12   0.00    0.0       !(R54)!EM
cyC6H9+C3H5=cyC6H8+C3H6      7.09E+12   0.00    3099.0    !(R55)!EM
!------------------------------cyC6H8-------------------------------------
cyC6H8 = cyC6H7 + H          5.01E+15   0.00    72598.0   !(R56)[4]
cyC6H8 = H2  + A1            2.36E+19   -1.4    67530.0   !(R57)[10]
!-----------------------cyC6H8 decomposition---------------------------------
cyC6H8+O2=cyC6H7+HO2         7.60E+12   0.00    25612.0   !(R58)!EM
cyC6H8+O=cyC6H7+OH           1.64E+12   0.00    2780.5    !(R59)!EM
cyC6H8+H=cyC6H7+H2           5.05E+13   0.00    2415.5    !(R60)!EM
cyC6H8+OH=cyC6H7+H2O         2.10E+13   0.00    0.0       !(R61)!EM
cyC6H8+HO2=cyC6H7+H2O2       1.47E+13   0.00    6540.5    !(R62)!EM
cyC6H8+HCO=cyC6H7+CH2O       1.46E+13   0.00    6433.5    !(R63)!EM
cyC6H8+CH3O=cyC6H7+CH3OH     1.58E+13   0.00    2459.7    !(R64)!EM
cyC6H8+CH3=cyC6H7+CH4        2.15E+13   0.00    2216.0    !(R65)!EM
cyC6H8+C2H5=cyC6H7+C2H6      1.84E+13   0.00    3343.0    !(R66)!EM
cyC6H8+C2H3=cyC6H7+C2H4      1.81E+13   0.00    658.0     !(R67)!EM
cyC6H8+C3H5=cyC6H7+C3H6      1.82E+13   0.00    6890.5    !(R68)!EM
!--------------------------Dehydrogenation cyC6H7-------------------------
cyC6H7=H+A1                  4.80E+25   -3.5    33480.0   !(R69)[10]
C2H2+i-C4H5=cyC6H7           3.16E+11   0.00    6000.0    !(R70)[11]
cyC6H7+O=C5H6+HCO            2.53E+13   0.00    0.0       !(R71)!EM
cyC6H7+HO2=>C5H6+HCO+OH      1.47E+13   0.00    0.0       !(R72)!EM
!-------------------------cyC6H7 decomposition-----------------------------
cyC6H7+O2=A1+HO2             7.61E+12   0.00    5244.7    !(R73)!EM
cyC6H7+O=A1+OH               1.27E+13   0.00    0.0       !(R74)!EM
cyC6H7+H=A1+H2               3.89E+13   0.00    0.0       !(R75)!EM
cyC6H7+OH=A1+H2O             1.23E+13   0.00    0.0       !(R76)!EM
cyC6H7+HO2=A1+H2O2           8.69E+12   0.00    0.0       !(R77)!EM
cyC6H7+HCO=A1+CH2O           8.12E+12   0.00    0.0       !(R78)!EM
cyC6H7+CH3O=A1+CH3OH         9.35E+12   0.00    0.0       !(R79)!EM
cyC6H7+CH3 =A1+CH4           1.10E+13   0.00    0.0       !(R80)!EM
cyC6H7+C2H5=A1+C2H6          9.45E+12   0.00    0.0       !(R81)!EM
cyC6H7+C2H3=A1+C2H4          9.31E+12   0.00    0.0       !(R82)!EM
cyC6H7+C3H5=A1+C3H6          1.82E+13   0.00    0.0       !(R83)!EM
!!!!!!!!!!!!!!!!!!!!!!!!!!!!LOW TEMPERATURE!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!---------------------------Addition-cyC6H11 with O2-----------------------
cyC6H11+O2=cyC6H11OO         8.00E+18  -2.5    0.0       !(R84)[12]*1.33
!-----------------------Isomerization of cyC6H11OO-------------------------
cyC6H11OO=cyC6H10OOH         2.00E+12   0.00   24045.0   !(R85)[13]*2/3
!---------------------------Decomposition of cyC6H10OOH--------------------
HO2+cyC6H10=cyC6H10OOH       8.00E+10   0.0    6000.0    !(R86)[11]
cyC6H10OOH=CH3CO+nC4H7+OH    3.00E+16   0.00   22500.0   !(R87)[14]_C8
cyC6H10OOH=CH2O+C5H8+OH      2.20E+16   0.00   22500.0   !(R88)[14]_C8
!------------Decomposition of cyC6H10OOH to cyclic ether & Ketone----------
cyC6H10OOH=OH+cyC6H10Oa      9.13E+09   0.60   8437.08   !(R89)!Reac-UQ
cyC6H10OOH=OH+cyC6H10Ob      1.25E+10   0.80   21662.2   !(R90)!Reac-UQ
cyC6H10OOH=OH+cyC6H10Oc      1.08E+12   0.60   23692.3   !(R91)!Reac-UQ
cyC6H10OOH=OH+cyC6H10Od      1.50E+09   0.00   7500.00   !(R92)[15]
!-----------------Addition-cyC6H10OOH with O2--------------------------------
cyC6H10OOH+O2=cyOOC6H10OOH   8.00E+18  -2.50   0.0     !(R93)!Anlg(R84)
!-----6-Isomerization of cyOOC6H10OOH & formation of keton hydroperoxy------
cyOOC6H10OOH=cyOOHC6H9OOH    3.00E+12  0.00   24045.0  !(R94)!Anlg(R85)
cyOOC6H10OOH=OH+cyOC6H9OOH   1.50E+16  0.00   42500.0  !(R95)[1] C8
cyOOHC6H9OOH=OH+cyOC6H9OOH   1.50E+9   0.00   7500.0   !(R96)!Anlg(R92)
```

```
!------------ H-atom abstraction-cylic ethers & cyclohexanone---------------
cyC6H10Oa+OH=cyC6H9O+H2O     3.71E+12  0.20   1133.5   !(R97)!Reac-UQ
cyC6H10Oa+HO2=cyC6H9O+H2O2   1.72E+11  0.50   16376.0  !(R98)!Reac-UQ
cyC6H10Oa+H=cyC6H9O+H2       1.01E+13  0.30   5210.0   !(R99)!Reac-UQ
cyC6H10Oa+CH3=cyC6H9O+CH4    2.51E+10  0.53   7524.0   !(R100)!Reac-UQ
!---------------H-atom abstraction-cyclic ethers & cyclohexanone-----------
cyC6H10Ob+OH=cyC6H9O+H2O     3.71E+12  0.20   1133.5   !(R101)!Anlg(R97)
cyC6H10Ob+HO2=cyC6H9O+H2O2   3.68E+11  0.50   16704.0  !(R102)!Reac-UQ
cyC6H10Ob+H=cyC6H9O+H2       1.01E+13  0.30   5210.0   !(R103)!Anlg(R99)
cyC6H10Ob+CH3=cyC6H9O+CH4    2.51E+10  0.53   7524.0   !(R104)!Anlg(R100)
!-------------------------------------------------------------------------
cyC6H10Oc+OH=cyC6H9O+H2O     3.63E+12  0.20   2940.0   !(R105)!Reac-UQ
cyC6H10Oc+HO2=cyC6H9O+H2O2   1.23E+11  0.50   16368.0  !(R106)!Reac-UQ
cyC6H10Oc+H=cyC6H9O+H2       9.53E+12  0.30   7010.0   !(R107)!Reac-UQ
cyC6H10Oc+CH3=cyC6H9O+CH4    3.43E+09  0.766  7534.0   !(R108)!Reac-UQ
!-------------------------------------------------------------------------
cyC6H10Od+OH =cyC6H9O+H2O    1.22E+13  0.00   5304.7   !(R109)!EM
cyC6H10Od+HO2=cyC6H9O+H2O2   1.14E+13  0.00   16279.7  !(R110)!EM
cyC6H10Od+H=cyC6H9O+H2       4.08E+13  0.00   8954.7   !(R111)!EM
cyC6H10Od+CH3=cyC6H9O+CH4    1.70E+13  0.00   8755.2   !(R112)!EM
!-------------------Decomposition of cyC6H9O ------------------------------
cyC6H9O=C2H4+C2H4+HCCO       7.00E+12  0.00  21900.0   !(R113)[16]
cyC6H9O=C2H3+C2H4+CH2CO      7.00E+12  0.00  21900.0   !(R114)[16]
i-C4H5+CH3CHO=cyC6H9O        1.00E+11  0.00  11900.0   !(R115)[1]_Type18
!------------------Decomposition of OcyC6H9OOH ----------------------------
cyOC6H9OOH=>CH3CH2O+CH2CHO+CH2CO  1.50E+16   0.00  42000.0   !(R116)[15]
!-----------------------Formation of cyC6H11O ------------------------------
cyC6H11OO+CH3O2=cyC6H11O+CH3O+O2          1.40e+16  -1.6  1860  !(R117)[1]
cyC6H11OO+cyC6H11OO=>cyC6H11O+cyC6H11O+O2 1.40e+16  -1.6  1860  !(R118)[1]
HO2+cyC6H11=cyC6H11O+OH                   7.00e+12  0.00  -1000 !(R119)[1]
!-------------------------Decomposition of cyC6H11O ------------------------
cyC6H11O=>C2H4+CH2CHO+C2H4   2.00E+13   0.00  25700.0  !(R120)[9]
cyC6H11O=>C2H3+C2H4+CH3CHO   2.00E+13   0.00  27700.0  !(R121)[9]
C5H9+CH2O=cyC6H11O           1.00E+11   0.00  11900.0  !(R122)[1]
!----------------------Pyrolyse of cyC6H10 -------------------------------
cyC6H9+O2=cyC6H9OO          8.00E+18   -2.5  0.0       !(R123)_Anlg(R84)
cyC6H9OO=cyC6H8OOH          3.00E+12   0.00  24045.0   !(R124)_Anlg(R85)
HO2+cyC6H8=cyC6H8OOH        8.00E+10   0.00  6000.0    !(R125)_Anlg(R86)
cyC6H8OOH=HCCO+nC4H7+OH     3.00E+16   0.00  22500.0   !(R126)_Anlg(R87)
cyC6H8OOH=CH2O+C5H6+OH      2.20E+16   0.00  22500.0   !(R127)_Anlg(R88)
!-------------------------------------------------------------------------
END
!*************************************************************************
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!PAH!!!!!!!!!!!!!!!!!!!!!!!
REACTIONS  MOLES  KELVINS
!*************************************************************************
!*************************************************************************
H2CCCH+C2H3 =  C5H5+H       9.600E+40  -7.80    14410.00
C5H5  =  H2CCCH + C2H2      5.00E+13    0.0     1.68E+04
C5H5+O2 =  CH2CO+C2H2+HCO   2.500E+19  -2.48    5480.00
C5H6+O2 =  C5H5+HO2         6.000E+13   0.00    12600.00
C5H5+O =  i-C4H5+CO         1.000E+14   0.00    0.00
C5H6+H =  C5H5+H2           5.600E+13   0.00    1137.00
C5H6+H =  C3H5+C2H2         3.200E+14   0.00    6200.00
C5H5+H =  C5H6              2.600E+14   0.00    0.00
C5H5+OH =  CH2O+2C2H2       1.000E+15   0.00    39000.00
C5H6+OH =  C5H5+H2O         3.430E+09   1.18    -225.00
C5H6+HO2 =  C5H5+H2O2       2.000E+12   0.00    5867.00
C5H6+C2H3 =  C5H5+C2H4      6.000E+12   0.00    0.00
```

```
C6H5O =  C5H5+CO            7.400E+11   0.00    22100.00
C6H5O+O =  C5H5+CO2         5.600E+13   0.00    0.00
C6H5O+H =  C5H6+CO          3.000E+13   0.00    0.00
C6H5O+H =  C6H5OH           2.500E+14   0.00    0.00
C6H5OH =  C5H6+CO           1.000E+12   0.00    30600.00
C6H5OH+O =  C6H5O+OH        2.800E+13   0.00    3600.00
C6H5OH+H =  C6H5O+H2        1.580E+13   0.00    3000.00
C6H5OH+OH =  C6H5O+H2O      6.000E+10   0.00    0.00
C6H5OH+C2H3 =  C6H5O+C2H4   6.000E+12   0.00    0.00
2H2CCCH =  A1               1.000E+36  -7.18    4234.00
2H2CCCH =  A1-+H            3.000E+35  -7.18    4234.00
H2CCCCH+C2H3 =  A1          3.000E+13   0.00    0.00
H2CCCCH+C2H3 =  A1-+H       6.000E+12   0.00    0.00
H2CCCH+C3H4 =  A1+H         1.400E+12   0.00    5000.00
C2H3+C4H4 =  A1+H           1.900E+12   0.00    1250.00
H2CCCCH+C2H2 =  A1-         5.000E+13   0.00    7450.00
C4H4+C2H2 =  A1-+H          1.000E+09   0.00    15000.00
i-C4H5+C2H2 =  A1+H         1.664E+23  -3.30    12509.0
i-C4H5+C2H3 =  A1+H2        1.800E-13   7.07   -1800.00
i-C4H5+C2H =  A1            1.000E+13   0.00    0.00
i-C4H5+C2H =  A1-+H         6.000E+12   0.00    0.00
C5H5+CH3 =  A1+2H           1.000E+18   0.00    30000.00
C5H6+C2H3 =  A1+CH3         2.120E+67  -16.08   21320.00
A1 =  A1-+H                 2.000E+17   0.00    55357.00
A1+O2 =  A1-+HO2            6.000E+13   0.00    31500.00
A1+O =  A1-+OH              2.000E+13   0.00    7400.00
A1+O =  C6H5OH              2.200E+13   0.00    2280.00
A1+O =  C6H5O+H             2.200E+13   0.00    2280.00
A1+H =  A1-+H2              2.510E+14   0.00    8060.00
A1+OH =  C6H5OH+H           0.650E+13   0.00    5280.00
A1+OH =  A1-+H2O            1.450E+13   0.00    2260.00
A1-+O2 =  C6H5O+O           2.600E+12   0.00    3050.00
A1-+O =  C5H5+CO            1.000E+14   0.00    0.00
A1-+OH =  C6H5O+H           5.000E+13   0.00    0.00
A1-+C6H5OH =  C6H5O+A1      4.910E+12   0.00    2200.00
i-C4H5+C3H4 =  C7H8+H       2.000E+12   0.00    1850.00
i-C4H5+H2CCCH =  C7H7+H     3.00E+12    0.00    0.0000
A1+CH2 =  C7H8              1.700E+13   0.00    4370.00
A1+CH2(S) =  C7H8           4.000E+13   0.00    4370.00
C7H8 =  A1-+CH3             1.400E+16   0.00    49900.00
i-C4H5+H2CCCH =  C7H8       3.000E+12   0.00    0.00000
C7H8+O2 =  C7H7+HO2         1.000E+14   0.00    20700.00
C7H8+O =  C7H7+OH           6.300E+11   0.00    0.00
C7H8+H =  A1+CH3            1.200E+13   0.00    2550.00
C7H8+H =  C7H7+H2           6.000E+13   0.00    4100.00
C7H8+OH =  C7H7+H2O         5.180E+09   1.00    440.000
C7H8+HO2 =  C7H7+H2O2       4.000E+11   0.00    7480.00
C7H8+CH3 =  C7H7+CH4        3.160E+12   0.00    5590.00
C7H8+C2H3 =  C7H7+C2H4      4.000E+12   0.00    4080.00
C7H8+H2CCCH =  C7H7+C3H4    1.600E+12   0.00    7580.00
C7H8+C3H5 =  C7H7+C3H6      5.000E+12   0.00    7480.00
C7H8+C5H5 =  C7H7+C5H6      1.600E+12   0.00    5580.00
C7H8+A1- =  C7H7+A1         7.940E+13   0.00    5596.00
!!!!!!!!!!!!!!Corrections to toluene combustion 18.10.2013!!!!!!!!
C7H8+C6H5O =  C7H7+C6H5OH    5.431E+12   0.00   10410.00
C7H8+HCO =  C7H7+CH2O        3.771E+13   0.00   11894.00
C7H8+i-C4H5 =  C7H7+C4H6     4.000E+12   0.00   3850.00
C7H7+H2CCCH =  C7H8+C3H2     1.000E+12   0.00   0.00
C7H7+HO2 =  A1-+CH2O+OH      1.170E+14   0.00   0.00
```

```
C7H7+O2 = A1-+HCO+OH         6.310E+12   0.00   21500.00
C7H7+HO2 = A1+HCO+OH         1.300E+13   0.00   550.00
C7H7+OH = A1-+CH2OH          1.200E+13   0.00   2574.00
A1-+CH3 =  C7H7+H            5.000E+13   0.00   0.00
C7H7 =  C4H4+H2CCCH          2.000E+15   0.00   42002.00
C7H7 =  C5H5+C2H2            2.000E+10   0.00   22371.00
C7H7+O =  A1+HCO             3.500E+13   0.00   0.00
C7H7+O =  A1-+CH2O           3.500E+13   0.00   0.00
C7H7+H =  C7H8               2.600E+14   0.00   0.00
C7H7+H+OH =  A1+CH2OH        1.200E+13   0.00   2592.00
i-C4H5+C4H2 =  A1C2H+H       3.160E+11   0.00   900.00
A1C2H-+H(+M) =  A1C2H(+M)    1.000E+14   0.00   0.00
    H2/2/H2O/6/CH4/2/CO/1.5/CO2/2/C2H6/3/
    LOW /6.600E+75 -16.30    7000.00 /
    TROE /1.0000E+00  1.0000E-01  5.8490E+02  6.1130E+03 /
H2CCCCH+C4H2 =  A1C2H-        9.600E+70   -17.77  15660.00
A1-+C4H2 =  A1C2H+C2H         2.000E+13    0.00   11000.00
A1-+C2H3 =  A1C2H+H2          7.900E+12    0.00   3200.00
A1-+C4H4 =  A1C2H+C2H3        3.200E+11    0.00   680.36
A1+C2H =  A1C2H+H             1.000E+12    0.00   0.00
A1-+C2H =  A1C2H              5.240E+14   -0.50   300.00
A1C2H+O =  A1C2H-+OH          1.100E+13    0.00   4100.00
A1C2H+O =  A1-+HCCO           2.100E+07    2.00   950.00
A1C2H+O =  C6H5O+C2H          2.200E+13    0.00   2260.00
A1C2H+H =  A1C2H-+H2          2.700E+13    0.00   4882.00
A1C2H+H =  A1-+C2H2           2.000E+14    0.00   4882.00
A1C2H+H =  n-C8H7             3.000E+43   -9.22   7612.00
A1C2H+OH =  A1C2H-+H2O        2.100E+13    0.00   2300.00
A1C2H+OH =  A1-+CH2CO         2.180E-04    4.50   -500.00
A1C2H+OH =  A1+HCCO           2.440E+03    3.02   5574.00
A1C2H+C2H =  A1C2H-+C2H2      2.000E+13    0.00   0.00
2C4H4 =  A1C2H3               1.800E+20   -1.90   20230.00
i-C4H5+C4H4 =  A1C2H3+H       3.160E+11    0.00   300.00
C5H5+H2CCCH =  A1C2H3*+H      3.000E+35   -7.18   4234.00
A1+C2H3 =  A1C2H3+H           7.900E+11    0.00   3200.00
A1-+C2H3 =  A1C2H3            1.060E+26   -4.00   2650.00
A1-+C2H4 =  A1C2H3+H          2.510E+12    0.00   3095.00
A1-+C4H4 =  A1C2H3+C2H        4.000E+13    0.00   10000.00
A1-+C4H6 =  A1C2H3+C2H3       3.200E+11    0.00   957.54
C7H7+CH2 =  A1C2H3+H          2.400E+14    0.00   0.00
A1C2H3+H =  n-C8H7+H2         6.650E+06    2.53   6120.00
A1C2H3+H =  A1C2H3*+H2        3.030E+02    3.30   2870.00
A1C2H3+O =  A1-+CH2HCO        3.000E+08    1.45   450.00
A1C2H3+O =  A1-+CH3+CO        1.920E+07    1.83   110.00
A1C2H3+O =  C2H3+C6H5O        2.200E+13    0.00   2265.00
A1C2H3+O =  n-C8H7+OH         7.550E+06    1.91   1880.00
A1C2H3+OH =  n-C8H7+H2O       3.100E+06    2.00   1715.00
A1C2H3+OH => C6H5O+C2H4       1.300E+13    0.00   5300.00
A1C2H3+OH =  A1C2H3*+H2O      1.630E+08    1.42   732.77
A1C2H3+OH =  C7H7+CH2O        1.400E+12    0.00   0.00
A1C2H3+O2 =  C6H5O+CH2HCO     1.880E+11    0.00   3758.70
A1C2H3*+O2 =  C6H5O+CH2CO     1.880E+12    0.00   3758.70
A1C2H3*+H(+M) =  A1C2H3(+M)   1.000E+14    0.00   0.00
    H2/2/H2O/6/CH4/2/CO/1.5/CO2/2/C2H6/3/
    LOW /6.600E+75 -16.30    7000.00 /
    TROE /1.0000E+00  1.0000E-01  5.8490E+02  6.1130E+03 /
C5H5+H2CCCH =  n-C8H7+H       1.500E+35   -7.18   4234.00
A1+C2H =  n-C8H7              7.000E+38   -8.02   8200.00
A1-+C2H2 =  n-C8H7            4.000E+13    0.00   5878.00
```

```
A1-+C2H3 =  n-C8H7+H          9.400E+00    4.14   11617.00
n-C8H7+H =  A1C2H3            5.400E+12    0.00   1210.00
n-C8H7+H =  A1C2H+H2          1.000E+13    0.00   0.00
n-C8H7+OH =  A1C2H+H2O        1.000E+13    0.00   0.00
C5H5+C4H4 =  INDENE+H         0.600E+12    0.00   5030.00
A1-+H2CCCH =  INDENE          3.860E+11    0.00   6850.47
C4H6 + A1- = INDENE+CH3       1.420E+13    0.00   14000.0
i-C4H5 + A1 = INDENE+CH3      1.420E+13    0.00   14000.0
A1-+C3H4 =  INDENE+H          1.000E+16    0.00   16600.00
C4H+C2H2 =  C6H2+H            2.3E+13      0.28   -37.00
2C3H2 =>  C6H2+H2             2.000E+13    0.00   42500.00
C6H+C2H2 =  C8H2+H            2.3E+13      0.28    -37.0
C2H+C6H2 =  C8H2+H            2.3E+13      0.28    -37.0
C4H2+C2H =  C4H+C2H2          2.000E+13    0.00    0.00
C4H2+C2H =  H+C6H2            2.3E+13      0.28    -37.0
2C4H2 =>  C8H2+2H             1.510E+14    0.00    28000.00
2C4H2 =  C8H2+H2              1.510E+13    0.00    21000.00
C6H2+M =  C6H+H+M             1.140E+17    0.00    68000.0
   AR/0.35/O2/0.4/CO/0.75/CO2/1.5/H2O/6.5/CH4/3/C2H6/3/
C6H2+H =  C6H+H2              7.700E+14   0.00     20000.00
C6H2+OH =  C6H+H2O            6.000E+13   0.00     7499.88
C6H2+C2H =  C4H+C4H2          1.000E+13   0.00     0.00
C8H2+M =  C8H+H+M             1.140E+17   0.00     68000.0
   AR/0.35/O2/0.4/CO/0.75/CO2/1.5/H2O/6.5/CH4/3/C2H6/3/
C8H2+H =  C8H+H2              7.700E+14   0.00     13000.00
C8H2+OH =  C8H+H2O            6.000E+13   0.00     6499.88
A1+CH3 =  A1-+CH4             2.000E+12   0.00     7530.00
A1+C2H =  A1-+C2H2            2.000E+13   0.00     0.00
A1+C4H =  A1-+C4H2            2.000E+13   0.00     0.00
A1+C6H =  A1-+C6H2            3.000E+13   0.00     0.00
A1+C8H =  A1-+C8H2            3.000E+13   0.00     0.00
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!NEW!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
INDENE+ O2 = INDENYL+HO2          2.00E+13     0.00    12500.00
INDENE+ HO2 = INDENYL+H2O2        2.00E+12     0.00    5829.35
INDENE =  INDENYL+H               1.100E+15    0.00    38800.00
INDENE+O =  INDENYL+OH            5.000E+13    0.00    0.00
INDENE+O =  C7H7+HCCO             2.000E+13    0.00    2000.00
INDENE+H =  INDENYL+H2            5.000E+13    0.00    0.00
C7H7+C2H2 =  INDENE+H             0.600E+12    0.00    5030.00
INDENE+H =  A1C2H+CH3             4.000E+14    0.00    23000.00
INDENE+H =  A1+H2CCCH             2.000E+14    0.00    24500.00
INDENE+OH =  C7H7+CH2CO           1.000E+13    0.00    5000.00
INDENE+OH =  INDENYL+H2O          5.000E+13    0.00    0.00
INDENE+CH3 =  INDENYL+CH4         1.000E+13    0.00    7000.00
INDENE+H2CCCH =  INDENYL+C3H4     7.800E+10    0.00    2770.15
INDENE+A1- =  INDENYL+A1          5.000E+11    0.00    3000.00
INDENE+C7H7 =  INDENYL+C7H8       1.000E+11    0.00    3500.00
C5H5+C4H2 = INDENYL               1.200E+12    0.00    5030.00
INDENYL => C2H2+C4H2+H2CCCH       1.000E+14    0.00    37500.00
INDENYL+O =  n-C8H7+CO            1.000E+14    0.00    0.00
INDENYL+O =  A1C2H3*+CO           1.000E+14    0.00    0.00
INDENYL+HO2 => n-C8H7+CO+OH       1.000E+13    0.00    0.00
INDENYL+HO2 => A1C2H+CO+H2O       1.000E+13    0.00    0.00
INDENYL+HO2 => A1C2H3*+CO+OH      1.000E+13    0.00    0.00
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!NEW!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
A1-+A1        =  P2+H               1.100E+23   -2.92    7450.00
INDENYL+H2CC => P2                  4.000E+11    0.00    7000.00
INDENE+H2CCC => P2+H                1.550E+14    0.00    25912.24
2A1-          =  P2                 2.000E+19   -2.05    1450.00
```

```
2A1-          =  P2-+H              2.300E-01    4.62    14500.00
P2            =  P2-+H              1.100E+19   -2.72    57300.00
P2            =  INDENE+C3H2        2.500E+14    0.00    55000.00
P2-+O2        =  A2+HCO+CO          2.000E+12    0.00    3700.00
P2+H          =  P2-+H2             2.500E+14    0.00    8000.00
P2+OH         =  P2-+H2O            1.600E+08    1.42    770.00
i-C4H5+A1     => A2+H2+H            1.600E+12    0.00    1503.48
C4H6+A1-      => A2+H2+H            5.000E+11    0.00    1503.48
A1-+H2CCCCH   =  A2                 3.180E+23   -3.20    2130.00
A1-+H2CCCCH   =  A2-+H              2.000E-10    7.10    786.19
A1-+C4H4      =  A2+H               3.300E+33   -5.70    12750.00
C7H7+H2CCCH   => A2+2H              2.000E+12    0.00    7000.00
A1C2H-+C2H2   =  A2-                4.000E+13    0.00    5100.00
A1C2H3*+C2H2  =  A2+H               1.600E+16   -1.33    3300.00
n-C8H7+C2H2   =  A2+H               1.600E+16   -1.33    2700.00
INDENYL+CH3   =  A2+2H              3.000E+18    0.00    36500.00
INDENE+CH2    => A2+2H              2.000E+13    0.00    4370.00
INDENE+CH2(S) =  A2+2H              4.000E+13    0.00    4370.00
A2+O          =  CH2CO+A1C2H        2.200E+13    0.00    2265.00
A2+O          => INDENYL+CO+H       3.600E+14    0.00    22093.00
A2+O          =  n-C8H7+HCCO        2.000E+13    0.00    21000.00
A2+O          =  A1C2H3*+HCCO       2.000E+13    0.00    21000.00
A2+O          =  A2-+OH             2.000E+13    0.00    7400.00
A2+H          =  A2-+H2             2.500E+14    0.00    8000.00
A2+OH         =  A2-+H2O            2.100E+13    0.00    2300.00
A2+OH         => A1C2H+CH2CO+H      1.300E+13    0.00    5300.00
A2+CH3        =  A2-+CH4            2.000E+12    0.00    7530.00
A2+C2H        =  A2-+C2H2           5.000E+13    0.00    8000.00
A2+C2H        =  A2C2H+H            5.000E+13    0.00    0.00
A2-+O2        => A1C2H+HCO+CO       2.000E+13    0.00    3700.00
A2-+O         => INDENYL+CO         1.000E+14    0.00    0.00
A2-+H         =  A2                 7.800E+13    0.00    0.00
A2-+HO2       => INDENYL+CO+OH      1.000E+13    0.00    0.00
A2-+C2H2      =  A2C2H+H            1.300E+24   -3.06    11300.00
A2C2H+H       =  A2C2H*+H2          2.500E+14    0.00    8000.00
A2C2H+OH      =  A2-+CH2CO          2.180E-04    4.50    -500.00
A2C2H+OH      =  A2C2H*+H2O         2.100E+13    0.00    2300.00
INDENYL+H2CCCH => A2C2H+2H          6.000E+11    0.00    0.00
A2-+CH3       =  A2CH3              3.050E+52  -11.80    8830.00
A2+CH2        =  A2CH3              2.200E+13    0.00    3680.00
A2+CH2(S)     =  A2CH3              4.400E+13    0.00    3680.00
A2CH2+H       =  A2CH3              1.000E+14    0.00    0.00
A2-+CH3       =  A2CH2+H            1.700E+36   -5.90    17315.00
A2CH3+O2      =  A2CH2+HO2          1.000E+14    0.00    20674.00
A2CH3+O       =  A2CH2+OH           5.000E+08    1.50    4000.00
A2CH3+H       =  A2CH2+H2           3.980E+02    3.44    1560.00
A2CH3+H       =  A2+CH3             8.670E+13    0.00    4045.00
A2CH3+OH      =  A2CH2+H2O          1.270E+12    0.00    1291.50
A2CH3+HO2     =  A2CH2+H2O2         4.000E+11    0.00    7037.00
A2CH3+CH3     =  A2CH2+CH4          1.580E+12    0.00    5549.70
A2CH3+A2-     =  A2CH2+A2           2.100E+12    0.00    2200.10
A2CH2+CH2     =  A2C2H+H2+H         2.400E+14    0.00    0.00
A2CH2+H2CCCH  =  A3+2H              4.000E+11    0.00    7000.00
A1C2H-+C4H4   =  A2R5+H             1.600E+16   -1.33    3300.00
A1C2H3*+C4H2  =  A2R5+H             1.600E+16   -1.33    2700.00
n-C8H7+C4H2   =  A2R5+H             1.600E+16   -1.33    2700.00
INDENYL+H2CCCH => A2R5+2H           8.300E+13    0.00    4888.30
INDENE+H2CCCH  => A2R5+H+H2         1.550E+14    0.00    25912.24
INDENYL+H2CCCH =  A2R5+H2           9.500E+12    0.00    0.00
```

```
A2-+C2H2       =  A2R5+H           1.900E+31  -5.26     10500.00
A2C2H*+H       =  A2R5             5.000E+13   0.00     0.00
A2C2H+H        =  A2R5+H           4.600E+37  -7.03     11550.00
A2R5-+H(+M)    =  A2R5(+M)         1.000E+14   0.00     0.00
 O2/0.4/ CO/0.75/ CO2/1.5/ H2O/6.5/ CH4/3/ C2H6/3/ AR/0.2/
    LOW /  6.600E+75 -16.30       3.50 /
    TROE /   1.0000E+00  1.0000E-01  5.8500E+02  6.1130E+03 /
A2R5           =  A1C2H+C4H2         5.000E+16    0.00    58000.00
A2R5+O         =  A2R5-+OH           2.000E+13    0.00    7400.00
A2R5+O         => A2-+HCCO           2.000E+13    0.00    7400.00
A2R5+H         =  A2R5-+H2           2.500E+14    0.00    8000.00
A2R5+OH        =  A2R5-+H2O          1.600E+08    1.42    725.00
A2R5+OH        =  A2-+CH2CO          1.000E+13    0.00    5000.00
A1C2H+A1-      =  A3+H               1.100E+23   -2.92    8010.00
A1C2H-+A1      =  A3+H               1.100E+23   -2.92    8010.00
A2-+C4H4       =  A3+H               3.300E+33   -5.70    12750.00
A2-+C4H2       =  A3-                3.300E+33   -5.70    12750.00
P2-+C2H2       =  A3+H               4.640E+06    1.97    3630.00
A2C2H*+C2H2    =  A3-                1.100E+62   -14.56   16550.00
A2R5-+C2H2     =  A3-                7.000E+37   -8.02    8200.00
A2R5+C2H2      => A3                 4.000E+04    2.45    14635.82
A2+C4H2        => A3                 2.765E+04    2.45    14635.82
A3+O           =  A2C2H+CH2CO        2.200E+13    0.00    2765.00
A3+O           =  A3-+OH             2.000E+13    0.00    7400.00
A3+O           => HCCO+P2-           2.000E+13    0.00    21000.00
A3+H           =  A3-+H2             2.500E+14    0.00    8000.00
A3+OH          =  A3-+H2O            1.700E+12    1.42    753.00
A3+OH          => A2C2H+CH2CO+H      1.300E+13    0.00    5000.00
A3+OH          =  CH2CO+P2-          4.000E+13    0.00    16000.00
A3+CH3         =  A3-+CH4            2.000E+12    0.00    7530.00
A3+C2H         =  A3C2H+H            5.000E+13    0.00    0.00
A3C2H+H        =  A3C2H*+H2          3.030E+02    3.30    2870.00
A3C2H+OH       =  A3-+CH2CO          2.180E-04    4.50    -500.00
A3-+O2         => CO+HCO+A2R5        2.000E+12    0.00    3700.00
A3-+H          =  A3                 1.000E+14    0.00    0.00
A3-+C2H2       =  A3C2H+H            1.200E+26   -3.44    15100.00
A3+CH2         =  A3CH3              2.200E+13    0.00    3596.00
A3+CH2(S)      =  A3CH3              4.200E+13    0.00    3596.00
A3CH2+H        =  A3-+CH3            1.000E+16    0.00    48800.00
A3CH3          =  A3CH2+H            2.810E+15    0.00    44700.00
A3CH3+O2       =  A3CH2+HO2          3.000E+14    0.00    20808.00
A3CH3+O        =  A3CH2+OH           1.200E+13    0.00    642.50
A3CH2+O        =  A3-+CH2O           1.650E+14    0.00    0.00
A3CH3+H        =  A3CH2+H2           1.200E+14    0.00    4200.00
A3CH3+H        =  A3+CH3             1.200E+13    0.00    2550.00
A3CH3+OH       =  A3CH2+H2O          1.260E+13    0.00    1275.00
A3CH3+HO2      =  A3CH2+H2O2         4.000E+11    0.00    7000.00
A3CH3+CH3      =  A3CH2+CH4          1.580E+12    0.00    5500.00
A3CH2+HO2      => A3-+CH2O+OH        8.000E+13    0.00    0.00
A3CH2+CH2      =  A4+H2+H            2.400E+14    0.00    0.00
C4H2+A2R5      => A4                 2.410E+02    2.23    -569.17
A1C2H+A1C2H-   =  A4+H               1.100E+24   -2.92    8010.00
n-C8H7+A1C2H   => A4+H2+H            1.100E+24   -2.92    8010.00
A1C2H3*+A1C2H  => A4+H2+H            1.100E+24   -2.92    8010.00
INDENYL+C7H7   => A4+2H2             4.300E+37   -6.30    22530.00
2INDENYL       => A4+C2H2+H2         4.300E+36   -6.30    22530.00
A2+C6H         =  A4-                7.000E+37   -8.02    8200.00
A2+A1-         =  A4+H+H2            1.000E+11    0.00    2500.00
A2-+A1         =  A4+H+H2            1.000E+12    0.00    2500.00
```

```
A2-+A1-        => A4+H2              4.300E+37   -6.30    22530.00
A2-+C6H2       =  A4-                7.000E+37   -8.02    8200.00
A2C2H*+C4H4    =  A4+H               3.300E+33   -5.70    12750.00
A2R5-+C4H2     => A4-                7.000E+37   -8.02    8200.00
A2R5-+H2CCCCH  =  A4                 6.400E+23   -3.20    2130.00
A3-+C2H2       =  A4+H               6.600E+24   -3.36    8900.00
A3C2H+H        =  A4+H               9.000E+38   -7.39    10400.00
A4+O           =  A3-+HCCO           2.000E+13    0.00    21000.00
A4+H           =  A4-+H2             2.500E+14    0.00    8000.00
A4+OH          =  A4-+H2O            1.700E+08    1.42    732.77
A4+OH          =  A3-+CH2CO          2.000E+13    0.00    21000.00
A4+CH3         =  A4-+CH4            3.030E+02    3.30    2870.00
A4-+O2         =  2CO+A3-            2.000E+12    0.00    3700.00
A4-+H          =  A4                 1.000E+14    0.00    0.00
A4-+C2H2       =  A4C2H+H            1.200E+26   -3.44    15100.00
A4C2H+H        =  A4C2H*+H2          2.500E+14    0.00    8000.00
A4C2H+H        =  BGHIF+H            4.600E+37   -7.03    11550.00
A4C2H*+H       =  BGHIF              5.000E+13    0.00    0.00
P2+C6H          =  C18H11            7.000E+37   -8.02    8200.00
P2-+C6H2        =  BGHIF+H           1.100E+24   -2.92    8010.00
P2-+C6H2        =  C18H11            7.000E+37   -8.02    8200.00
A3-+C4H4        =  C18H12+H          3.300E+33   -5.70    12750.00
A3C2H*+C2H2     =  BGHIF+H           1.600E+16   -1.33    3300.00
A1C2H-+A2       => BGHIF+H2+H        2.100E+25   -2.92    8010.00
A1C2H+A2-       => BGHIF+H2+H        2.100E+25   -2.92    8010.00
INDENE+INDENYL  => C18H12+H2+H       1.100E+23   -2.92    8010.00
2INDENYL        => BGHIF+2H2         8.300E+38   -6.30    22530.00
A2C2H+A1-       =  C18H12+H          1.100E+24   -2.92    8010.00
A2C2H*+A1       =  C18H12+H          1.100E+24   -2.92    8010.00
A2R5-+A1        => BGHIF+H2+H        1.100E+25   -2.92    8010.00
A3C2H*+C4H4     =  BAPYR+H           3.300E+33   -5.70    12750.00
A4-+C4H4        =  BAPYR+H           3.300E+33   -5.70    12750.00
A4C2H*+C2H2     =  BAPYR*S           7.000E+37   -8.02    8200.00
BAPYR*S+H       =  BAPYR             1.000E+14    0.00    0.00
P2+A1C2H-       => BAPYR+H2+H        1.100E+24   -2.92    8010.00
P2-+A1C2H3*     => BAPYR+2H2         8.300E+38   -6.30    22530.00
P2-+n-C8H7      => BAPYR+2H2         8.300E+38   -6.30    22530.00
A2R5-+A1C2H-    =  BAPYR             8.300E+38   -6.30    22530.00
A2R5+A1C2H-     =  BAPYR+H           2.100E+25   -2.92    8010.00
A2R5-+A1C2H     =  BAPYR+H           2.100E+25   -2.92    8010.00
C18H11+O2       => HCO+CO+A4         2.000E+13    0.00    3700.00
C18H11+H        =  BGHIF+H2          1.000E+14    0.00    0.00
C18H11+C2H      => BAPYR             5.240E+14   -0.50    350.00
C18H11+C2H2     =  BAPYR+H           2.100E+24   -3.36    8900.00
C18H12+O        =  C18H11+OH         2.000E+13    0.00    7400.00
C18H12+H        =  C18H11+H2         3.030E+02    3.30    2870.00
C18H12+OH       =  C18H11+H2O        1.700E+08    1.42    732.77
BGHIF+O         =  HCCO+A4-          2.000E+13    0.00    7400.00
BGHIF+OH        =  CH2CO+A4-         1.300E+13    0.00    5300.00
BAPYR*S+O2      => HCO+CO+BGHIF      2.000E+13    0.00    3700.00
C4H2+A4         => BAPYR             7.000E+02    2.23    -569.17
BAPYR+O         =  HCCO+C18H11       2.000E+13    0.00    21000.00
BAPYR+OH        => CH2CO+C18H11      1.300E+13    0.00    5300.00
2C5H5           => A2+2H             3.000E+16    0.00    23625.00
  DUPLICATE
2C5H5           => A2+2H             4.530E+05    1.83    18041.00
  DUPLICATE
C5H5+H2CCCH     =  A1C2H3            1.000E+13    0.00    4174.00
C5H5+H2CCCCH    =  INDENE            1.000E+13    0.00    4174.00
```

```
2C5H5          =  INDENYL+CH3       2.500E+12    0.00    4811.00
C5H6+CH3       =  C5H5+CH4          1.000E-01    4.00    0.00
C5H5+C5H6      =  INDENE+CH3        9.630E+13    1.63    29972.00
n-C8H7+A1C2H-  => A4+2H             3.000E+17    0.00    23625.00
INDENYL+C5H5   => A3+2H             3.000E+17    0.00    23625.00
2INDENYL       => C18H12+2H         6.000E+17    0.00    23625.00
A1C2H3*+A1C2H- =  A4+2H             6.000E+17    0.00    23625.00
A2C2H*+n-C8H7  =  BAPYR+2H          6.000E+17    0.00    23625.00
A2C2H*+A1C2H3* =  BAPYR+2H          6.000E+17    0.00    23625.00
A2R5-+A1-      => BGHIF+2H          6.000E+16    0.00    23625.00
P2-+A1C2H-     => BAPYR+2H          6.000E+17    0.00    23625.00
A1C2H3+CH3     =  A1C2H3*+CH4       2.000E+12    0.00    7530.00
A2R5+CH3       =  A2R5-+CH4         2.000E+12    0.00    7530.00
P2+CH3         =  P2-+CH4           2.000E+12    0.00    7530.00
A1+O           =  C5H6+CO           5.800E+16   -0.77    7645.00
A2R5+OH        => A2+HCCO           1.760E+02    3.25    2795.20
A1C2H3*+CH3    =  INDENE+H2         3.000E+18    0.00    36500.00
C7H7+CH3       =  A1C2H3+H2         1.060E+26   -4.00    2650.00
END
```


[1]. H.J.Curran, Combust Flame 129 (2002) 253-80.
[2]. Ristori A, Dagaut P, El Bakali A, Cathonnet M, Combust.Sci.Tech., Vol. 165, 2001, pp. 197-228.
[3]. Tsang et al., Inter. J. Chem. Kinet. 20 (1978) Thermal Stability of Cyclohexane and 1-Hexene
[4]. Voisin D, Marchal A, Reuillon M, Boettner JC, Cathonnet M, Combust.Sci.Tech., Vol. 138, 1998, pp. 137-158.
[5]. Zhang HR, Huynh LK, Kungwan N, Yang Z, Zhang S, J. Phys. Chem. A, Vol. 111, 2007, pp. 4102-4115.
[6]. Sirjean B, Buda F, Hakka H, Glaude PA, Fournet R, Warth V, Battin-Lecler F, Lopez MR, Proc. Combust. Inst., Vol. 31, 2007, pp. 277-284.
[7]. Cohen et al., J. Chem. Kint 14 (1982) 1339-1362_TableV
[8]. Sirjean B, Glaude PA, Ruiz-Lopèz MF, Fournet R, J. Phys. Chem. A,Vol. 112, 2008, No.46, pp. 11598-11610.
[9]. Dayma G, Glaude, PA, Fournet R, Battin-Leclerc F, Int. J. Chem. Kin., Vol. 35, No. 7, 2003, pp. 273-285
[10]. Orme, JP, Curran, HJ, Simmie, JM ,J. Phys. Chem. A, 2006, 110 (1), pp 114–131.
[11]. Silke, EJ, Pitz, W. J., Westbrook, C. K., Ribaucour, M., J. Phys. Chem. A, Vol. 111, 2007, pp. 3761-3775.
[12]. F Buda, R Bounaceur, V Warth, PA Glaude, R Fournet, F Battin-Leclerc,Combust. Flame 142 (2005) 170–186.
[13]. Granata S, Faravelli T, Ranzi E,Combustion & Flame, Vol. 132, 2003, pp. 533-544.
[14]. Ranzi E, Faravelli T, Gaffuri P, Sogaro A, Combustion & Flame, Vol. 108, 1997, pp. 24-42.
[15]. Serinyel Z, Herbinet O, Frottier O, Dirrenberger P, Warth V, Glaude PA, Battin-Leclerc F, Combustion & Flame, Vol. 160, 2013, pp. 2319-2332.
[16]. G. E. Bogin, E. Osecky, M.A. Ratcliff, J. Luecke, X. He, B. T. Zigler, A. M. Dean, "Ignition Quality Tester (IQT) Investigation of the Negative Temperature Coefficient Region of Alkane Autoignition," Energy & Fuels, vol. 27, pp. 1632-1642, 2013.

Appendix II

Thermochemistry data (thermdat)

```
THERMO
   300.000  1000.000  5000.000
H2  REF ELEMENT   RUS 78H   2    0    0    0G   200.000  6000.000 1000.       1
 0.29328305E+01 0.82659802E-03-0.14640057E-06 0.15409851E-10-0.68879615E-15    2
-0.81305582E+03-0.10243164E+01 0.23443029E+01 0.79804248E-02-0.19477917E-04    3
 0.20156967E-07-0.73760289E-11-0.91792413E+03 0.68300218E+00 0.00000000E+00    4
CH4    RRHO       g 8/99C   1H   4    0    0G   200.000  6000.000 1000.       1
 1.91178600E+00 9.60267960E-03-3.38387841E-06 5.38797240E-10-3.19306807E-14    2
-1.00992136E+04 8.48241861E+00 5.14825732E+00-1.37002410E-02 4.93749414E-05    3
-4.91952339E-08 1.70097299E-11-1.02453222E+04-4.63322726E+00-8.97226656E+03    4
C2H2 acetylene    g 1/91C   2H   2    0    0G   200.000  6000.000 1000.       1
 4.65878489E+00 4.88396667E-03-1.60828888E-06 2.46974544E-10-1.38605959E-14    2
 2.57594042E+04-3.99838194E+00 8.08679682E-01 2.33615762E-02-3.55172234E-05    3
 2.80152958E-08-8.50075165E-12 2.64289808E+04 1.39396761E+01 2.74459950E+04    4
C2H4              g 1/00C   2H   4    0    0G   200.000  6000.000 1000.       1
 3.99182724E+00 1.04833908E-02-3.71721342E-06 5.94628366E-10-3.53630386E-14    2
 4.26865851E+03-2.69081762E-01 3.95920063E+00-7.57051373E-03 5.70989993E-05    3
-6.91588352E-08 2.69884190E-11 5.08977598E+03 4.09730213E+00 6.31426266E+03    4
C2H6              g 8/88C   2H   6    0    0G   200.000  6000.000 1000.       1
 4.04666411E+00 1.53538802E-02-5.47039485E-06 8.77826544E-10-5.23167531E-14    2
-1.24473499E+04-9.68698313E-01 4.29142572E+00-5.50154901E-03 5.99438458E-05    3
-7.08466469E-08 2.68685836E-11-1.15222056E+04 2.66678994E+00-1.00849652E+04    4
C3H4                    H   4C   3    0    0G   200.00   6000.00  1000.00     01
 6.31687220E+00 1.11337280E-02-3.96293780E-06 6.35642380E-10-3.78755400E-14    2
 2.01174950E+04-1.09957660E+01 2.61304450E+00 1.21225750E-02 1.85398800E-05    3
-3.45251490E-08 1.53350790E-11 2.15415670E+04 1.02261390E+01                   4
C3H6                    H   6C   3    0    0G   300.00   5000.00  1000.00     01
 6.72139740E+00 1.49317570E-02-4.96523530E-06 7.25107530E-10-3.80014760E-14    2
-9.24531490E+02-1.21556170E+01 1.45751570E+00 2.11422630E-02 4.04680120E-06    3
-1.63190030E-08 7.04751530E-12 1.07402080E+03 1.73994600E+01                   4
C4H2                    H   2C   4    0    0G   200.00   6000.00  1000.00     01
 8.66700350E+00 6.71663710E-03-2.35449950E-06 3.73830790E-10-2.21189140E-14    2
 4.98569330E+04-2.11142050E+01-3.95185080E-01 5.19558130E-02-9.17866160E-05    3
 8.05239290E-08-2.69170880E-11 5.14517090E+04 2.09691010E+01                   4
C4H4  1-butene-3  T06/04C   4H   4    0    0G   200.000  6000.000 1000.       1
 7.98456038E+00 1.20558816E-02-4.23587475E-06 6.73646140E-10-3.99059864E-14    2
 3.11993029E+04-1.67958975E+01 1.37368786E+00 2.88801256E-02-1.46863874E-05    3
-3.91045446E-09 4.78133572E-12 3.30633344E+04 1.75941274E+01 3.46213066E+04    4
C4H6  1,3-butadienT05/04C   4H   6    0    0G   200.000  6000.000 1000.       1
 7.62637466E+00 1.72523403E-02-6.09184911E-06 9.70800102E-10-5.76169721E-14    2
 9.55306395E+03-1.48325259E+01 4.10599669E+00 5.05575563E-03 5.83885454E-05    3
-8.05950198E-08 3.27447711E-11 1.15092468E+04 8.42978067E+00 1.33302095E+04    4
nC4H7 3-buten-1-ylT05/04C  4.H  7.   0.   0.G   200.000  6000.000 1000.       1
 8.49073768E+00 1.91056974E-02-6.74370664E-06 1.07343267E-09-6.36251837E-14    2
 2.04659294E+04-1.74555814E+01 5.07355313E+00 5.27619329E-03 6.23441322E-05    3
-8.54203458E-08 3.45890031E-11 2.24615054E+04 5.60318035E+00 2.46070249E+04    4
C4H8 tr2-butene   T 5/09C  4.H  8.   0.   0.G   200.000  6000.000 1000.       1
 7.89114667E+00 2.24970532E-02-8.12143779E-06 1.31273568E-09-7.84451632E-14    2
-5.51643171E+03-1.76436027E+01 5.57278967E+00 3.76541017E-03 6.52226708E-05    3
-8.30909522E-08 3.20311342E-11-3.60128327E+03 5.37796708E-01-1.34523863E+03    4
C3H8                    H   8C   3    0    0G    300.00   5000.00 1000.00     01
 7.53413680E+00 1.88722390E-02-6.27184910E-06 9.14756490E-10-4.78380690E-14    2
-1.64675160E+04-1.78923490E+01 9.33553810E-01 2.64245790E-02 6.10597270E-06    3
-2.19774990E-08 9.51492530E-12-1.39585200E+04 1.92016910E+01                   4
```

```
O2 REF ELEMENT    RUS 89O   2    0    0    0G   200.000  6000.000 1000.       1
 3.66096083E+00 6.56365523E-04-1.41149485E-07 2.05797658E-11-1.29913248E-15    2
-1.21597725E+03 3.41536184E+00 3.78245636E+00-2.99673415E-03 9.84730200E-06    3
-9.68129508E-09 3.24372836E-12-1.06394356E+03 3.65767573E+00 0.00000000E+00    4
C2                    C   2    0    0    0G    200.00   6000.00 1000.00     01
 3.79137060E+00 5.16504730E-04-2.54869600E-08-8.22635540E-12 1.00861680E-15    2
 9.90230590E+04 2.81518020E+00 8.64705500E-01 3.93531200E-02-1.19818180E-04    3
 1.39081030E-07-5.52055030E-11 9.87313030E+04 1.15301410E+01                   4
H2O               L 5/89H   2O   1    0    0    0G   200.000  6000.000 1000.       1
 0.26770389E+01 0.29731816E-02-0.77376889E-06 0.94433514E-10-0.42689991E-14    2
-0.29885894E+05 0.68825500E+01 0.41986352E+01-0.20364017E-02 0.65203416E-05    3
-0.54879269E-08 0.17719680E-11-0.30293726E+05-0.84900901E+00-0.29084817E+05    4
H2O2              T 8/03H  2.O  2.   0.   0.G   200.000  6000.000 1000.       1
 4.57977305E+00 4.05326003E-03-1.29844730E-06 1.98211400E-10-1.13968792E-14    2
-1.80071775E+04 6.64970694E-01 4.31515149E+00-8.47390622E-04 1.76404323E-05    3
-2.26762944E-08 9.08950158E-12-1.77067437E+04 3.27373319E+00-1.63425145E+04    4
CO                RUS 79C   1O   1    0    0G   200.000  6000.000 1000.       1
 0.30484859E+01 0.13517281E-02-0.48579405E-06 0.78853644E-10-0.46980746E-14    2
-0.14266117E+05 0.60170977E+01 0.35795335E+01-0.61035369E-03 0.10168143E-05    3
 0.90700586E-09-0.90442449E-12-0.14344086E+05 0.35084093E+01-0.13293628E+05    4
CO2               L 7/88C   1O   2    0    0G   200.000  6000.000 1000.       1
 0.46365111E+01 0.27414569E-02-0.99589759E-06 0.16038666E-09-0.91619857E-14    2
-0.49024904E+05-0.19348955E+01 0.23568130E+01 0.89841299E-02-0.71220632E-05    3
 0.24573008E-08-0.14288548E-12-0.48371971E+05 0.99009035E+01-0.47328105E+05    4
CH2O              L 8/88H   2C   1O   1    0G   200.000  6000.000 1000.       1
 0.31694807E+01 0.61932742E-02-0.22505981E-05 0.36598245E-09-0.22015410E-13    2
-0.14478425E+05 0.60423533E+01 0.47937036E+01-0.99081518E-02 0.37321459E-04    3
-0.37927902E-07 0.13177015E-10-0.14308955E+05 0.60288702E+00-0.13059098E+05    4
CH2CO             T 6/94C   2H   2O   1    0G   200.000  6000.000 1000.       1
 0.57577901E+01 0.63496507E-02-0.22584407E-05 0.36208462E-09-0.21569030E-13    2
-0.79786113E+04-0.61064037E+01 0.21401165E+01 0.18088368E-01-0.17324216E-04    3
 0.92767477E-08-0.19915011E-11-0.70430509E+04 0.12198699E+02-0.57366700E+04    4
CH3CHO                 H   4O   1C   2    0G    200.00   6000.00 1000.00     1
 5.40411080E+00 1.17230590E-02-4.22631370E-06 6.83724510E-10-4.09848630E-14    2
-2.25931220E+04-3.48079170E+00 4.72945950E+00-3.19328580E-03 4.75349210E-05    3
-5.74586110E-08 2.19311120E-11-2.15728780E+04 4.10301590E+00                   4
C                 L 7/88C   1    0    0    0G   200.000  6000.000 1000.       1
 0.26055830E+01-0.19593434E-03 0.10673722E-06-0.16423940E-10 0.81870580E-15    2
 0.85411742E+05 0.41923868E+01 0.25542395E+01-0.32153772E-03 0.73379223E-06    3
-0.73223487E-09 0.26652144E-12 0.85442681E+05 0.45313085E+01 0.86195097E+05    4
H                 L 6/94H   1    0    0    0G   200.000  6000.000 1000.       1
 0.25000000E+01 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 0.25473660E+05-0.44668285E+00 0.25000000E+01 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 0.25473660E+05-0.44668285E+00 0.26219035E+05    4
CH                IU3/03C   1H   1    0    0G   200.000  6000.000 1000.       1
 0.25209369E+01 0.17653639E-02-0.46147660E-06 0.59289675E-10-0.33474501E-14    2
 0.70994878E+05 0.74051829E+01 0.34897583E+01 0.32432160E-03-0.16899751E-05    3
 0.31628420E-08-0.14061803E-11 0.70660755E+05 0.20842841E+01 0.71706297E+05    4
CH2 TRIPLET       IU3/03C   1H   2    0    0G   200.000  6000.000 1000.       1
 3.14631886E+00 3.03671259E-03-9.96474439E-07 1.50483580E-10-8.57335515E-15    2
 4.60412605E+04 4.72341711E+00 3.71757846E+00 1.27391260E-03 2.17347251E-06    3
-3.48858500E-09 1.65208866E-12 4.58723866E+04 1.75297945E+00 4.70502772E+04    4
CH2(S) SINGLET    IU3/03C  1.H  2.   0.   0.G   200.000  6000.000 1000.       1
 3.13501686E+00 2.89593926E-03-8.16668090E-07 1.13572697E-10-6.36262835E-15    2
 5.05040504E+04 4.06030621E+00 4.19331325E+00-2.33105184E-03 8.15676451E-06    3
-6.62985981E-09 1.93233199E-12 5.03662246E+04-7.46734310E-01 5.15724919E+04    4
```

```
CH3                     H   3C   1    0    0G    200.00   6000.00 1000.00    0 1
 2.97812060E+00 5.79785200E-03-1.97558000E-06 3.07297900E-10-1.79174160E-14    2
 1.65095130E+04 4.72247990E+00 3.65717970E+00 2.12659790E-03 5.45838830E-06    3
-6.61810030E-09 2.46570740E-12 1.64227160E+04 1.67353540E+00                   4
C2H ETHYNYL RAD   T07/00C   2H   1    0    0G   200.000  6000.000 1000.        1
 3.66459586E+00 3.82189487E-03-1.36509398E-06 2.13253692E-10-1.23098939E-14    2
 6.72238503E+04 3.91355399E+00 2.90180321E+00 1.32859725E-02-2.80508233E-05    3
 2.89300812E-08-1.07446930E-11 6.71171170E+04 6.17234595E+00 6.83770805E+04    4
C2H3  Vinyl Radi  ATcT/AC  2.H  3.   0.   0.G   200.000  6000.000 1000.        1
 4.15026763E+00 7.54021341E-03-2.62997847E-06 4.15974048E-10-2.45407509E-14    2
 3.38566380E+04 1.72812235E+00 3.36377642E+00 2.65765722E-04 2.79620704E-05    3
-3.72986942E-08 1.51590176E-11 3.44749589E+04 7.91510092E+00 3.56701718E+04    4
C2H5                    H   5C   2    0    0G    200.00   3500.00 1000.00    0 1
 1.95465642E+00 1.73972722E-02-7.98206668E-06 1.75217689E-09-1.49641576E-13    2
 1.28575200E+04 1.34624343E+01 4.30646568E+00-4.18658892E-03 4.97142807E-05    3
-5.99126606E-08 2.30509004E-11 1.28416265E+04 4.70720924E+00                   4
C3H2                    H   2C   3    0    0G    200.00   6000.00 1000.00    0 1
 5.69445684E+00 6.53821901E-03-2.35907266E-06 3.82037384E-10-2.29227460E-14    2
 5.49264274E+04-6.96163733E+00 3.18167129E+00-3.37611741E-04 3.95343765E-05    3
-5.49792422E-08 2.28335240E-11 5.61816758E+04 9.06482468E+00                   4
H2CCCH                  H   3C   3    0    0G    200.00   6000.00 1000.00    0 1
 7.14221880E+00 7.61902005E-03-2.67459950E-06 4.24914801E-10-2.51475415E-14    2
 3.80693414E+04-1.25848435E+01 1.35110927E+00 3.27411223E-02-4.73827135E-05    3
 3.76309808E-08-1.18540923E-11 3.92663770E+04 1.52058924E+01                   4
H2CCCCH                 H   3C   4    0    0G    298.15   6000.00 1000.00    0 1
 8.47620790E+00 8.87823270E-03-3.03284120E-06 4.73583020E-10-2.77166270E-14    2
 5.47565400E+04-1.71705510E+01 2.41732470E+00 2.41047820E-02-1.28134700E-05    3
-2.86062370E-09 3.91945270E-12 5.65064760E+04 1.44711070E+01                   4
C3H5                    H   5C   3    0    0G    200.00   6000.00 1000.00    0 1
 7.41036790E+00 1.27002380E-02-4.60067840E-06 7.46810500E-10-4.48759790E-14    2
 1.63749060E+04-1.50083170E+01 3.11350850E+00 9.90763750E-03 3.22193340E-05    3
-4.96732560E-08 2.06446380E-11 1.82618420E+04 1.06902410E+01                   4
i-C4H5 2-Buyn-1yl T10/06C   4H   5    0    0G   200.000  6000.000 1000.        1
 7.62618778E+00 1.47321922E-02-5.22511622E-06 8.36085367E-10-4.97358383E-14    2
 3.33816425E+04-1.26664026E+01 4.41575788E+00 1.36823548E-02 1.76533170E-05    3
-3.06168262E-08 1.27850098E-11 3.47871254E+04 6.39669972E+00 3.68133184E+04    4
O                  L 1/90O   1    0    0    0G   200.000  6000.000 1000.        1
 2.54363697E+00-2.73162486E-05-4.19029520E-09 4.95481845E-12-4.79553694E-16    2
 2.92260120E+04 4.92229457E+00 3.16826710E+00-3.27931884E-03 6.64306396E-06    3
-6.12806624E-09 2.11265971E-12 2.91222592E+04 2.05193346E+00 2.99687009E+04    4
OH                      H   1O   1    0    0G    200.00   6000.00 1000.00    0 1
 2.83853033E+00 1.10741289E-03-2.94000209E-07 4.20698729E-11-2.42289890E-15    2
 3.69780808E+03 5.84494652E+00 3.99198424E+00-2.40106655E-03 4.61664033E-06    3
-3.87916306E-09 1.36319502E-12 3.36889836E+03-1.03998477E-01                   4
HO2                L 5/89H   1O   2    0    0G   200.000  6000.000 1000.        1
 4.17228741E+00 1.88117627E-03-3.46277286E-07 1.94657549E-11 1.76256905E-16    2
 3.10206839E+01 2.95767672E+00 4.30179807E+00-4.74912097E-03 2.11582905E-05    3
-2.42763914E-08 9.29225225E-12 2.64018485E+02 3.71666220E+00 1.47886045E+03    4
HCO                T 5/03C  1.H  1.O  1.   0.G   200.000  6000.000 1000.        1
 3.92001542E+00 2.52279324E-03-6.71004164E-07 1.05615948E-10-7.43798261E-15    2
 3.65342928E+03 3.58077056E+00 4.23754610E+00-3.32075257E-03 1.40030264E-05    3
-1.34239995E-08 4.37416208E-12 3.87241185E+03 3.30834869E+00 5.08749163E+03    4
CH3O  METHOXY RAD IU1/03C  1.H  3.O  1.   0.G   200.000  6000.000 1000.        1
 4.75779238E+00 7.44142474E-03-2.69705176E-06 4.38090504E-10-2.63537098E-14    2
 3.90139164E+02-1.96680028E+00 3.71180502E+00-2.80463306E-03 3.76550971E-05    3
-4.73072089E-08 1.86588420E-11 1.30772484E+03 6.57240864E+00 2.53773223E+03    4
```

```
CH2OH RADICAL     IU2/03C  1.H  3.O  1.   0.G   200.000  6000.000 1000.        1
 5.09312037E+00 5.94758550E-03-2.06496524E-06 3.23006703E-10-1.88125052E-14    2
-4.05813228E+03-1.84690613E+00 4.47832317E+00-1.35069687E-03 2.78483707E-05    3
-3.64867397E-08 1.47906775E-11-3.52476728E+03 3.30911984E+00-2.06867272E+03    4
HCCO              T 6/94C   2H   1O   1    0G   200.000  6000.000 1000.        1
 0.58469006E+01 0.36405960E-02-0.12959007E-05 0.20796919E-09-0.12400022E-13    2
 0.19248496E+05-0.52916533E+01 0.23350118E+01 0.17010083E-01-0.22018867E-04    3
 0.15406447E-07-0.43455097E-11 0.20050299E+05 0.11976729E+02 0.21336387E+05    4
CH2HCO                  H   3O   1C   2    0G    300.00   5000.00 1000.00    0 1
 5.31371650E+00 9.17377930E-03-3.32203860E-06 5.39474560E-10-3.24523680E-14    2
-3.64504140E+03-1.67575580E+00 4.03587050E+00 8.77294870E-04 3.07100100E-05    3
-3.92475650E-08 2.86738510E-12 1.52147660E+03 9.55829050E+00                   4
CH3CO                   H   3O   1C   2    0G    200.00   6000.00 1000.00    0 1
 5.94477310E+00 7.86672050E-03-2.88658820E-06 4.72708750E-10-2.85998610E-14    2
-3.78730750E+03-5.01367510E+00 4.16342570E+00-2.32616100E-04 3.42678200E-05    3
-4.41052270E-08 1.72756120E-11-2.65745290E+03 7.34682800E+00                   4
N2                      N   2    0    0    0G    200.00   6000.00 1000.00    0 1
 2.95254070E+00 1.39688380E-03-4.92625770E-07 7.86000910E-11-4.60749780E-15    2
-9.23937530E+02 5.87182210E+00 3.53096280E+00-1.23659500E-04-5.02993390E-07    3
 2.43527680E-09-1.40879540E-12-1.04696370E+03 2.96743910E+00                   4
AR                      AR  1    0    0    0G    300.00   5000.00 1000.00    0 1
 2.50000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
-7.45375000E+02 4.36600000E+00 2.50000000E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-7.45375000E+02 4.36600000E+00                   4
A1   BENZENE       g 6/01C   6H   6    0    0G   200.000  6000.000 1000.        1
 1.10809576E+01 2.07176746E-02-7.52145991E-06 1.22320984E-09-7.36091279E-14    2
 4.30641035E+03-4.00413310E+01 5.04818632E-01 1.85020642E-02 7.38345881E-05    3
-1.18135741E-07 5.07210429E-11 8.55247913E+03 2.16412893E+01 9.96811598E+03    4
A1-   PHENYL RAD  T04/02C   6H   5    0    0G   200.000  6000.000 1000.        1
 1.08444762E+01 1.73212473E-02-6.29233249E-06 1.02369961E-09-6.16216828E-14    2
 3.55598475E+04-3.53735134E+01 2.10306633E-01 2.04745507E-02 5.89743006E-05    3
-1.01534255E-07 4.47105660E-11 3.95468722E+04 2.52910455E+01 4.08610970E+04    4
C6H5OH phenol     g 8/00C  6.H  6.O  1.   0.G   200.000  6000.000 1000.        1
 1.41552427E+01 1.99350340E-02-7.18219540E-06 1.16229002E-09-6.97147483E-14    2
-1.81287441E+04-5.17984911E+01-2.90978575E-01 4.08562397E-02 2.42829425E-05    3
-7.14477617E-08 3.46002146E-11-1.34129780E+04 2.68745637E+01-1.15940687E+04    4
C6H5O  Phenoxy    T05/02C  6.H  5.O  1.   0.G   200.000  6000.000 1000.        1
 1.37221720E+01 1.74688771E-02-6.35504520E-06 1.03492308E-09-6.23410504E-14    2
 2.87274751E+02-4.88181680E+01-4.66204455E-01 4.13443975E-02 1.32412991E-05    3
-5.72872769E-08 2.89763707E-11 4.77858391E+03 2.76990274E+01 6.49467016E+03    4
C5H5 CY           T12/89C   5H   5    0    0G   200.000  6000.000 1000.        1
 0.10844072E+02 0.15392831E-01-0.55630422E-05 0.90189440E-09-0.54156619E-13    2
 0.26950886E+05-0.35254983E+02-0.95902849E+00 0.31396777E-01 0.26724050E-04    3
-0.68942183E-07 0.33301983E-10 0.30779441E+05 0.29072780E+02 0.32004580E+05    4
C5H6              T 1/90C   5H   6    0    0G   200.000  6000.000 1000.        1
 0.99757848E+01 0.18905543E-01-0.68411461E-05 0.11099340E-08-0.66680236E-13    2
 0.11081693E+05-0.32209454E+02 0.86108957E+00 0.14804031E-01 0.72108895E-04    3
-0.11338055E-06 0.48689972E-10 0.14801755E+05 0.21353453E+02 0.16152485E+05    4
A1C2H C6H5CCH     T12/06C  8.H  6.   0.   0.G   200.000  6000.000 1000.        1
 1.63582907E+01 2.11974105E-02-7.65817215E-06 1.24134505E-09-7.45327960E-14    2
 3.10375340E+04-6.22520227E+01-2.74707918E+00 7.78284438E-02-6.69709932E-05    3
 2.37972496E-08-8.43279765E-13 3.61131008E+04 3.54221257E+01 3.82082350E+04    4
C7H8              L 6/87C   7H   8    0    0G  200.000  6000.000               1
 0.12940034E+02 0.26691287E-01-0.96838505E-05 0.15738629E-08-0.94663601E-13    2
-0.69764908E+03-0.46728785E+02 0.16152663E+01 0.21099438E-01 0.85366018E-04    3
-0.13261066E-06 0.55956604E-10 0.40756300E+04 0.20282210E+02 0.60135835E+04    4
```

```
A1C2H3            T12/94C   8H   8    0    0G   298.150  5000.000              1
 0.16139277E+02 0.24210847E-01-0.72678359E-05 0.11392276E-08-0.72984881E-13    2
 0.10249251E+05-0.61169437E+02-0.10717708E+02 0.12666725E+00-0.17762493E-03    3
 0.14344049E-06-0.47616577E-10 0.16597133E+05 0.71526331E+02 0.17723291E+05    4
A1C2H3*                H   7C   8    0    0G    300.00   3000.00 1000.00    0 1
 1.15635990E+01 3.02108100E-02-1.15455930E-05 1.73023200E-09-5.23797650E-14    2
 4.04984920E+04-3.48829650E+01-3.88686850E+00 6.81689610E-02-3.48058750E-05    3
-5.64102540E-09 8.07147580E-12 4.49413590E+04 4.59431880E+01                   4
n-C8H7            T 2/99C   8H   7    0    0G   200.000  6000.000              1
 1.80458471E+01 2.21498794E-02-8.05082743E-06 1.30961070E-09-7.88615885E-14    2
 3.87090843E+04-7.17917960E+01-8.85283632E-01 5.61565120E-02 1.16600084E-05    3
-6.99146159E-08 3.63590274E-11 4.45850990E+04 2.97497087E+01 4.67991499E+04    4
C7H7              T08/90C   7H   7    0    0G  200.000  6000.000               1
 0.14043980E+02 0.23493873E-01-0.85375367E-05 0.13890841E-08-0.83614420E-13    2
 0.18564203E+05-0.51665589E+02 0.48111540E+00 0.38512832E-01 0.32861492E-04    3
-0.76972721E-07 0.35423068E-10 0.23307027E+05 0.23548820E+02 0.25317186E+05    4
A1C2H-   C6H4CCH  H6W/94C   8H   5    0    0G   300.000  3000.000              1
 1.23595010E+01 2.54533570E-02-1.06065540E-05 1.89146030E-09-1.06306220E-13    2
 6.09304610E+04-4.09002080E+01-4.44958590E+00 7.69950670E-02-6.66170380E-05    3
 2.50386820E-08-1.97566010E-12 6.52259260E+04 4.44279480E+01                   4
A2 Naphthalene    T 7/98C  10H   8    0    0G   200.000  6000.000              1
 1.86129884E+01 3.04494175E-02-1.11224825E-05 1.81615474E-09-1.09601281E-13    2
 8.91578988E+03-8.00230396E+01-1.04919475E+00 4.62970781E-02 7.07591636E-05    3
-1.38408111E-07 6.20475407E-11 1.59848987E+04 3.02121626E+01 1.81107678E+04    4
A2-   Naphtyl rad T 7/98C  10H   7    0    0G   200.000  6000.000              1
 1.83535073E+01 2.77474314E-02-1.00885968E-05 1.64229575E-09-9.89002001E-14    2
 3.89261241E+04-7.48978150E+01-1.89559772E+00 5.83077290E-02 2.79388931E-05    3
-9.14375172E-08 4.46422302E-11 4.55409775E+04 3.52453263E+01 4.76546183E+04    4
INDENE            T 9/96C   9H   8    0    0G   200.000  6000.000              1
 0.17318671E+02 0.28982768E-01-0.10605059E-04 0.17334553E-08-0.10467919E-12    2
 0.11151429E+05-0.71555323E+02-0.68190289E+00 0.41658733E-01 0.70741234E-04    3
-0.13430875E-06 0.59915845E-10 0.17705036E+05 0.29781396E+02 0.19741190E+05    4
INDENYL           T 9/96C   9H   7    0    0G   200.000  6000.000              1
 0.18554959E+02 0.25035076E-01-0.91457509E-05 0.14934838E-08-0.90133030E-13    2
 0.25721156E+05-0.76300347E+02-0.26698729E+01 0.62177216E-01 0.15067018E-04    3
-0.79645699E-07 0.40918972E-10 0.32386969E+05 0.37861193E+02 0.34349570E+05    4
P2  BIPHENYL      L12/84C  12H  10    0    0G  300.000  5000.000               1
 0.24289017E 02 0.34006648E-01-0.11722408E-04 0.17729298E-08-0.96812532E-13    2
 0.10287000E 05-0.10802374E 03-0.40739527E 01 0.86973310E-01-0.42353613E-05    3
-0.64564460E-07 0.34150169E-10 0.19405965E 05 0.44741348E 02 0.21905340E 05    4
P2-                    H   9C  12    0    0G   300.00  5000.00  1000.00     0 1
 0.23851303E 02 0.31960227E-01-0.11076719E-04 0.16847825E-08-0.92641173E-13    2
 0.40171297E 05-0.10270549E 03-0.31376228E 01 0.82217276E-01-0.40171444E-05    3
-0.60809782E-07 0.32074482E-10 0.48868754E 05 0.42730362E 02 0.51444448E 05    4
A2C2H*                 H   7C  12    0    0G   300.00   3000.00 1000.00     0 1
 1.33715110E+01 4.99657190E-02-2.62269020E-05 6.59494350E-09-6.45885050E-13    2
 6.84904150E+04-4.64872350E+01-6.25389030E+00 1.14753010E-01-1.05430910E-04    3
 4.79127480E-08-7.92157250E-12 7.32491920E+04 5.19412620E+01                   4
A2R5  ACENAPHTH   T12/00C  12H   8    0    0G   300.000  5000.000              1
 1.93183637E+01 3.90205238E-02-1.63352587E-05 3.10041991E-09-2.19199281E-13    2
 2.15445149E+04-8.32372261E+01-2.81264181E+00 7.04681002E-02 3.15341955E-05    3
-1.05176189E-07 5.08713845E-11 2.88462829E+04 3.75755975E+01 3.12345526E+04    4
A2C2H  C10H7-CCH  T 7/98C  12H   8    0    0G   200.000  6000.000              1
 2.34108373E+01 3.12979308E-02-1.13777419E-05 1.85217551E-09-1.11546889E-13    2
 3.49196941E+04-1.00594596E+02-2.59169367E+00 8.63306190E-02-1.76590976E-05    3
-5.26006488E-08 3.15924760E-11 4.27720678E+04 3.73574503E+01 4.55914299E+04    4
```

```
A2R5-                   H   7C  12    0    0G   300.00   3000.00 1000.00     0 1
 1.19534280E+01 5.23860720E-02-2.76952570E-05 6.98583910E-09-6.84938560E-13    2
 5.31995200E+04-4.03924920E+01-7.33802680E+00 1.11965800E-01-9.32829450E-05    3
 3.58663420E-08-4.26602220E-12 5.80597670E+04 5.73507140E+01                   4
A3     PHENANTHRE T 1/94C  14H  10    0    0G   200.000  6000.000              1
 0.26602474E+02 0.39769744E-01-0.14572026E-04 0.23843296E-08-0.14409548E-12    2
 0.12132838E+05-0.12266672E+03-0.33646717E+01 0.85073271E-01 0.37531110E-04    3
-0.12664499E-06 0.61445705E-10 0.22019878E+05 0.40596218E+02 0.24908263E+05    4
A3-   4-Phenantr  T11/07C  14H   9    0    0G   298.150  5000.000              1
 2.68173412E+01 3.76935761E-02-1.45586251E-05 2.58486800E-09-1.73198001E-13    2
 4.14405846E+04-1.21547559E+02-1.08929968E+01 1.41537035E-01-1.14205532E-04    3
 3.57710437E-08 0.00000000E+00 5.21136455E+04 7.37137024E+01 5.42184687E+04    4
A4      PYRENE    T10/96C  16H  10    0    0G   200.000  6000.000              1
 0.29910014E+02 0.42668069E-01-0.15733834E-04 0.25851725E-08-0.15667980E-12    2
 0.12786491E+05-0.14186953E+03-0.40420321E+01 0.91549657E-01 0.51443344E-04    3
-0.15276576E-06 0.73087530E-10 0.24094241E+05 0.43665312E+02 0.27145316E+05    4
A4-        4/25/97 THERMC  16H   9    0    0G   300.000  5000.000 1370.000    01
 3.52580112E+01 3.37799342E-02-1.20577497E-05 1.92626216E-09-1.14006421E-13    2
 4.10224476E+04-1.72843003E+02-2.70728686E+00 1.13309510E-01-7.24420479E-05    3
 2.13864176E-08-2.29813560E-12 5.51266878E+04 3.43198885E+01                   4
C18H12 CHR 4/19/97 THERMC  18H  12    0    0G   300.000  5000.000 1673.000    01
 3.31662137E+01 5.08795514E-02-1.87182202E-05 3.06104765E-09-1.84366391E-13    2
 1.57642287E+04-1.59238481E+02 3.12629742E+00 1.06385095E-01-4.82700462E-05    3
 5.22816930E-09 1.05961625E-12 2.69644034E+04 6.40602579E+00                   4
C18H11     4/19/97 THERMC  18H  11    0    0G   300.000  5000.000 1553.000    01
 3.80927732E+01 4.14888957E-02-1.46997248E-05 2.33682189E-09-1.37836631E-13    2
 4.31156376E+04-1.86409947E+02 7.63557478E+00 8.20163654E-02-1.33888864E-05    3
-1.71944312E-08 6.31097097E-12 5.66581749E+04-1.21249371E+01                   4
A3C2H                   H  10C  16    0    0G    300.00   3000.00 1000.00    0 1
 5.21651460E+01-1.31973180E-02 3.43530560E-05-1.62838920E-08 2.36773620E-12    2
 3.42350550E+04-2.54066510E+02-1.16026740E+01 1.68243940E-01-1.64320300E-04    3
 8.63943800E-08-1.93105670E-11 5.21728360E+04 7.55153660E+01                   4
A3C2H*                  H   9C  16    0    0G    300.00   3000.00 1000.00    0 1
 4.42042910E+01 1.00322200E-02 5.84986920E-06-3.10823390E-09 3.90443000E-13    2
 6.74150930E+04-2.11916320E+02-1.05579250E+01 1.69544630E-01-1.86994930E-04    3
 1.20985220E-07-3.56159160E-11 8.28806100E+04 7.09147620E+01                   4
C4H               T12/91C   4H   1    0    0G   200.000  6000.000              1
 0.77680939E+01 0.49850386E-02-0.17648839E-05 0.28217408E-09-0.16779623E-13    2
 0.93912126E+05-0.14159577E+02 0.13210657E+01 0.38562824E-01-0.71343174E-04    3
 0.65319977E-07-0.22607050E-10 0.95021629E+05 0.15554575E+02 0.96617600E+05    4
C4                      C   4    0    0    0G    200.00   6000.00 1000.00    0 1
 5.63077100E+00 4.83138180E-03-1.50416810E-06 2.02894600E-10-1.00360920E-14    2
 1.22500940E+05-2.98873090E+00 3.32277500E+00 2.02592340E-02-3.73452130E-05    3
 3.56859090E-08-1.27718610E-11 1.22723640E+05 6.80979580E+00                   4
C6H2              T 3/92C   6H   2    0    0G   200.000  6000.000              1
 0.12532801E+02 0.87766321E-02-0.31329616E-05 0.50371820E-09-0.30071921E-13    2
 0.79784338E+05-0.38858580E+02-0.54109216E+00 0.74532628E-01-0.13578252E-03    3
 0.12226630E-06-0.41825207E-10 0.82115132E+05 0.21882710E+02 0.84288792E+05    4
C8H2              T 2/92C   8H   2    0    0G   298.150  5000.000              1
 0.17007524E+02 0.93656848E-02-0.30485718E-05 0.47653534E-09-0.29169032E-13    2
 0.10628021E+06-0.59224564E+02 0.12470437E+01 0.78392526E-01-0.12416148E-03    3
 0.98381697E-07-0.30063943E-10 0.10942891E+06 0.16048227E+02 0.11236828E+06    4
C6H               T 3/92C   6H   1    0    0G   200.000  6000.000              1
 0.11361786E+02 0.75157820E-02-0.27216114E-05 0.43917513E-09-0.26217995E-13    2
 0.12080112E+06-0.29989833E+02 0.10110111E+01 0.59781961E-01-0.10773934E-03    3
 0.96196601E-07-0.32681317E-10 0.12261638E+06 0.17998104E+02 0.12479773E+06    4
```

```
C8H               T 2/92C   8H   1    0    0G   298.150  5000.000             1
 0.17422244E+02 0.66413688E-02-0.22557166E-05 0.36657347E-09-0.23188722E-13    2
 0.13376514E+06-0.59275082E+02 0.34566807E+01 0.65220393E-01-0.98141367E-04    3
 0.72046762E-07-0.20447036E-10 0.13656779E+06 0.77719815E+01 0.13976290E+06    4
A4C2H      5/ 2/97 THERMC  18H  10    0    0G   300.000  5000.000 1380.000    01
 4.00549856E+01 3.70780570E-02-1.31321889E-05 2.08714093E-09-1.23089687E-13    2
 3.54491810E+04-1.96221074E+02-1.66684897E+00 1.29146981E-01-8.88321137E-05    3
 2.96510612E-08-3.87600847E-12 5.04370421E+04 2.97034755E+01                   4
A4C2H*     5/ 2/97 THERMC  18H   9    0    0G   300.000  5000.000 1376.000    01
 3.95503456E+01 3.50980873E-02-1.24815028E-05 1.98905158E-09-1.17522532E-13    2
 6.60214976E+04-1.91256136E+02-4.46464976E-01 1.21677939E-01-8.16502810E-05    3
 2.61409743E-08-3.21316409E-12 8.05697723E+04 2.59457844E+01                   4
BAPYR*S  4/24/97 THERM  H  11C  20    0    0G    300.00   5000.00 1367.00    0 1
 4.42864852E+01 4.17445643E-02-1.48863371E-05 2.37663494E-09-1.40600809E-13    2
 4.29850608E+04-2.21959150E+02-3.62587203E-01 1.30524557E-01-7.53627823E-05    3
 1.75825498E-08-8.69471980E-13 5.99859990E+04 2.32559064E+01                   4
BGHIF  4/24/97 THERM    H  10C  18    0    0G    300.00   5000.00 1397.00    0 1
 4.03484789E+01 3.60369349E-02-1.25974449E-05 1.98535622E-09-1.16421390E-13    2
 2.33917123E+04-2.03794640E+02-1.35024568E+01 1.75273343E-01-1.52006334E-04    3
 6.58323068E-08-1.13175755E-11 4.05739002E+04 8.03624456E+01                   4
BAPYR  4/24/97 THERM    H  12C  20    0    0G    300.00   5000.00 1373.00    0 1
 4.46587811E+01 4.38683433E-02-1.55934247E-05 2.48422256E-09-1.46748672E-13    2
 1.24605731E+04-2.25482194E+02-2.08146408E+00 1.40317388E-01-8.64400516E-05    3
 2.37333999E-08-2.15247872E-12 2.99280993E+04 3.00065203E+01                   4
A2CH3 C10H7-CH3   T 7/98C  11H  10    0    0G   200.000  6000.000             1
 2.17939213E+01 3.60214098E-02-1.33228698E-05 2.19304403E-09-1.33071380E-13    2
 3.16261439E+03-9.48675403E+01-1.03043715E+00 6.03358177E-02 5.45655719E-05    3
-1.22769251E-07 5.54507327E-11 1.13241014E+04 3.22970611E+01 1.39642625E+04    4
A2CH2 C10H7-CH2*  T 7/98C  11H   9    0    0G   200.000  6000.000             1
 2.18977539E+01 3.26102636E-02-1.18401218E-05 1.92574628E-09-1.15903442E-13    2
 2.24571098E+04-9.41050741E+01-2.53234304E+00 7.32920338E-02 2.02974707E-05    3
-9.36547823E-08 4.70753594E-11 3.02906705E+04 3.79638513E+01 3.28097266E+04    4
A3CH3      5/ 3/97 THERMC  15H  12    0    0G   300.000  5000.000 2025.000    11
 2.86721901E+01 4.57935671E-02-1.67466881E-05 2.72794395E-09-1.63863026E-13    2
 6.77859249E+03-1.31269124E+02 2.45407326E-01 1.03437006E-01-5.52427842E-05    3
 1.17708807E-08-4.92994185E-13 1.69368456E+04 2.37077261E+01                   4
A3CH2      5/ 3/97 THERMC  15H  11    0    0G   300.000  5000.000 2030.000    11
 2.95619587E+01 4.24589619E-02-1.55841596E-05 2.54481062E-09-1.53124916E-13    2
 2.56273028E+04-1.36219923E+02 1.33783643E-01 1.04067922E-01-5.92362501E-05    3
 1.43179766E-08-9.91637313E-13 3.59458944E+04 2.35063505E+01                   4
HE REF ELEMENT    L10/90HE  1    0    0    0G   200.000  6000.000 1000.       1
 2.50000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
-7.45375000E+02 9.28723974E-01 2.50000000E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-7.45375000E+02 9.28723974E-01 0.00000000E+00    4
C2H5O2H           T10/96C   2H   6O   2    0G   200.000  6000.00  1000.0      1
 9.99511555E+00 1.47311626E-02-5.30621235E-06 8.58442516E-10-5.14814807E-14    2
-2.53850722E+04-2.53504050E+01 4.37310002E+00 1.04422436E-02 4.63854723E-05    3
-7.02772770E-08 2.93034879E-11-2.29362227E+04 8.30134323E+00-2.08834916E+04    4
C2H5O2                  C   2H   5O   20   00   300.00   5000.00  1000.00     1
 0.78275410E+01 0.15347060E-01-0.58108700E-05 0.10465070E-08-0.71520540E-13    2
-0.45527100E+04-0.12726800E+02 0.39390180E+01 0.13991490E-01 0.21720800E-04    3
-0.36137480E-07 0.14824910E-10-0.28469040E+04 0.10394470E+02                   4
C2H5O             T11/82O   1C   2H   5    0G   300.000  5000.0   1000.0      1
 0.60114346E+01 0.12165219E-01-0.40449604E-05 0.59076588E-09-0.30969595E-13    2
-0.49366992E+04-0.67901798E+01 0.17302504E+01 0.16908489E-01 0.39996221E-05    3
-0.13711180E-07 0.57643603E-11-0.32922483E+04 0.17336115E+02-0.20138288E+04    4
```

```
C2H5OH            L 8/88C   2H   6O   1    0G   200.000  6000.00  1000.0       1
 0.65624365E+01 0.15204222E-01-0.53896795E-05 0.86225011E-09-0.51289787E-13    2
-0.31525621E+05-0.94730202E+01 0.48586957E+01-0.37401726E-02 0.69555378E-04    3
-0.88654796E-07 0.35168835E-10-0.29996132E+05 0.48018545E+01-0.28257829E+05    4
CH3CHOH                C   2H   5O   1     G    300.00   5000.00 1553.00      1
 .726570301E+01 .109588926E-01-.363662803E-05 .553659830E-09-.317012322E-13    2
-.864371441E+04-.106822851E+02 .183974631E+01 .187789371E-01-.460544253E-05    3
-.213116990E-08 .943772653E-12-.629595195E+04 .201446141E+02                   4
CH3CH2O            MAR96C   2H   5O   1     G  0300.00   5000.00  1405.00     1
 8.31182392E+00 1.03426319E-02-3.39186089E-06 5.12212617E-10-2.91601713E-14    2
-6.13097954E+03-2.13985581E+01-2.71296378E-01 2.98839812E-02-1.97090548E-05    3
 6.37339893E-09-7.77965054E-13-3.16397196E+03 2.47706003E+01                   4
CH2CHO            T04/83O   1H   3C   2    0G   300.000  5000.000   1000.0     1
 0.59756699E+01 0.81305914E-02-0.27436245E-05 0.40703041E-09-0.21760171E-13    2
 0.49032178E+03-0.50320879E+01 0.34090624E+01 0.10738574E-01 0.18914925E-05    3
-0.71585831E-08 0.28673851E-11 0.15214766E+04 0.95714535E+01 0.30474436E+04    4
HOC2H4O2               C   2H   5O   3    0G   300.000  5000.    1395.00      1
 9.22339915E+00 1.41346358E-02-4.75283025E-06 7.28795964E-10-4.18969629E-14    2
-2.35984031E+04-1.53847386E+01 3.58811609E+00 2.99414161E-02-2.35156549E-05    3
 1.12635525E-08-2.28663686E-12-2.17409435E+04 1.42166729E+01                   4
CH2CH2OH               C   2H   5O   1     G    300.00   5000.00 1391.00      1
 .752244726E+01 .110492715E-01-.372576465E-05 .572827397E-09-.330061759E-13    2
-.729337464E+04-.124960750E+02 .117714711E+01 .248115685E-01-.150299503E-04    3
 .479006785E-08-.640994211E-12-.495369043E+04 .220081586E+02                   4
C2H5OH            L 8/88C   2H   6O   1    0G   200.000  6000.00  1000.0       1
 0.65624365E+01 0.15204222E-01-0.53896795E-05 0.86225011E-09-0.51289787E-13    2
-0.31525621E+05-0.94730202E+01 0.48586957E+01-0.37401726E-02 0.69555378E-04    3
-0.88654796E-07 0.35168835E-10-0.29996132E+05 0.48018545E+01-0.28257829E+05    4
CH3OH             L 8/88C   1H   4O   1     G   200.000  3500.000  1000.000    1
 1.78970791E+00 1.40938292E-02-6.36500835E-06 1.38171085E-09-1.17060220E-13    2
-2.53748747E+04 1.45023623E+01 5.71539582E+00-1.52309129E-02 6.52441155E-05    3
-7.10806889E-08 2.61352698E-11-2.56427656E+04-1.50409823E+00                   4
C2H3CHO                H   4O   1C   3    0G   300.000  5000.000 1393.000    11
 1.04184959E+01 9.48963321E-03-3.29310529E-06 5.16279203E-10-3.01587291E-14    2
-1.49630281E+04-3.07235061E+01 2.92355162E-01 3.54321417E-02-2.94936324E-05    3
 1.28100124E-08-2.26144108E-12-1.16521584E+04 2.28878280E+01                   4
C3H6CHO                C   4H  07O   1    0G   300.00  3000.000  1000.0       1
 0.15884652E+01 0.38848859E-01-0.20962528E-04 0.52620127E-08-0.49851983E-12    2
-0.36434795E+04 0.22754273E+02 0.11187767E+01 0.50216809E-01-0.50689131E-04    3
 0.34205034E-07-0.10624679E-10-0.41594220E+04 0.22377984E+02-0.19809959E+04    4
C3H5CHO   4/9/14       C   4H  06O   1    0G   300.00  3000.000  1000.0       1
 0.74028426E+01 0.25027017E-01-0.11694960E-04 0.26087291E-08-0.22523544E-12    2
-0.13924496E+05-0.10163097E+02 0.15817174E+01 0.31958802E-01 0.44541101E-05    3
-0.29658106E-07 0.14779730E-10-0.11886571E+05 0.22045862E+02-0.10008420E+05    4
C2H4CHO   4/9/14       C   3H  05O   1    0G   300.00  3000.000  1000.0       1
 0.16172502E+02-0.24872866E-02 0.64772222E-05-0.25806195E-08 0.31271116E-12    2
-0.42357344E+04-0.57124588E+02 0.32458902E+01 0.21862943E-01-0.21551078E-05    3
-0.11090728E-07 0.60560358E-11 0.37206752E+03 0.13536087E+02 0.22720712E+04    4
C3H6OH     4/24/92 THERMC   3H   7O   1    0G   300.000  5000.000 1403.000    31
 1.09340809E+01 1.49384611E-02-4.97490474E-06 7.58435125E-10-4.34420191E-14    2
-1.15876725E+04-2.89343754E+01 1.65867207E-01 4.13141037E-02-2.99664397E-05    3
 1.16234591E-08-1.86270510E-12-7.97925983E+03 2.84481654E+01                   4
O2C3H6OH   4/24/92 THERMC   3H   7O   3    0G   300.000  5000.000 1380.000    41
 1.55655181E+01 1.68822736E-02-5.91144639E-06 9.32274430E-10-5.46815496E-14    2
-2.95301139E+04-5.17312137E+01 2.20217327E+00 4.59913087E-02-3.03766163E-05    3
 1.05366009E-08-1.55928684E-12-2.45762626E+04 2.09594636E+01                   4
```

```
C3H5O2     4/24/92 THERMC   3H   5O   2    0G   300.000  5000.000 1370.000    21
 1.27832465E+01 1.25399349E-02-4.43433905E-06 7.03952842E-10-4.14804136E-14    2
 5.58979899E+03-4.03574985E+01 2.65293041E+00 3.19993514E-02-1.73652420E-05    3
 4.00148647E-09-2.51071126E-13 9.58815244E+03 1.56431929E+01                   4
C3H5O2H    4/24/92 THERMC   3H   6O   2    0G   300.000  5000.000 1386.000    31
 1.39009363E+01 1.34732295E-02-4.70091523E-06 7.39632892E-10-4.33128479E-14    2
-1.29274765E+04-4.49719922E+01 1.75161845E+00 4.16542055E-02-3.01268606E-05    3
 1.14209488E-08-1.80624472E-12-8.64152220E+03 2.04277976E+01                   4
C3H5O      4/24/92 THERMC   3H   5O   1    0G   300.000  5000.000 1375.000    21
 9.93380796E+00 1.21383493E-02-4.23299952E-06 6.65805507E-10-3.89817563E-14    2
 6.20904655E+03-2.68841926E+01 1.48979417E+00 2.77306345E-02-1.35044719E-05    3
 2.24225811E-09 8.28232368E-14 9.58557792E+03 1.99841620E+01                   4
nC3H7O2    4/24/92 THERMC   3H   7O   2    0G   300.000  5000.000 1376.000    31
 1.39295562E+01 1.62109297E-02-5.69426414E-06 8.99917649E-10-5.28613664E-14    2
-1.09646348E+04-4.81871702E+01 1.65182379E+00 4.10402887E-02-2.41422856E-05    3
 6.91955127E-09-7.89713852E-13-6.22330250E+03 1.92752981E+01                   4
nC3H7O2H   4/24/92 THERMC   3H   8O   2    0G   300.000  5000.000 1392.000    31
 1.45695935E+01 1.77104023E-02-6.09654929E-06 9.50484279E-10-5.53030086E-14    2
-2.92401303E+04-4.99984239E+01 6.27002549E-01 5.14448631E-02-3.83791359E-05    3
 1.54653552E-08-2.61561123E-12-2.44385400E+04 2.45962330E+01                   4
iC3H7O2    4/24/92 THERMC   3H   7O   2    0G   300.000  5000.000 1382.000    31
 1.45333419E+01 1.56502508E-02-5.48993478E-06 8.66859600E-10-5.08886097E-14    2
-1.33000915E+04-5.13639953E+01 1.03606539E+00 4.57999209E-02-3.15792877E-05    3
 1.14069765E-08-1.73998862E-12-8.39327437E+03 2.17529616E+01                   4
iC3H7O2H   4/24/92 THERMC   3H   8O   2    0G   300.000  5000.000 1395.000    31
 1.51552007E+01 1.71807437E-02-5.90648731E-06 9.20033944E-10-5.34977754E-14    2
-3.15766321E+04-5.30871350E+01 1.35497567E-01 5.55626488E-02-4.48202480E-05    3
 1.93393698E-08-3.43326450E-12-2.66246790E+04 2.65182104E+01                   4
iC3H7O       cc      cc C   3H   7O   1    0G   300.000  5000.000 1379.000    21
 1.24938036E+01 1.42024822E-02-4.76949687E-06 7.32349424E-10-4.21933677E-14    2
-1.25023025E+04-4.32454233E+01-1.45132586E-01 4.09328495E-02-2.46708437E-05    3
 6.60628776E-09-5.34569348E-13-7.91212088E+03 2.54949227E+01                   4
nC3H7O N-PROPOXY  T 3/96C   3H   7O   1    0G   298.150  5000.00  1000.0      1
 0.84124958E+01 0.19520193E-01-0.71317071E-05 0.12393621E-08-0.82483889E-13    2
-0.87750718E+04-0.18293360E+02 0.91452571E+00 0.33601264E-01-0.12282254E-04    3
-0.10739947E-08 0.72924952E-12-0.61847956E+04 0.22563171E+02-0.45289500E+04    4
iC3H7 i-propyl    A 5/05C   3H   7    0    0G   200.000  6000.000 1000.       1
 5.30597255E+00 1.89854588E-02-6.74315384E-06 1.07993730E-09-6.42785036E-14    2
 7.78748910E+03-2.23233935E+00 5.47421257E+00-8.42536682E-03 8.04607759E-05    3
-9.49287824E-08 3.59830971E-11 9.04939013E+03 3.40542323E+00 1.08473019E+04    4
nC3H7           N-L 9/84C   3H   7    0    0G   300.000  5000.00  1000.0      1
 0.77026987E 01 0.16044203E-01-0.52833220E-05 0.76298590E-09-0.39392284E-13    2
 0.82984336E 04-0.15480180E 02 0.10515518E 01 0.25991980E-01 0.23800540E-05    3
-0.19609569E-07 0.93732470E-11 0.10631863E 05 0.21122559E 02 0.12087447E 05    4
iC4H7 1-meth-allylT05/04C  4.H  7.   0.   0.G   200.000  6000.000 1000.       1
 8.08107449E+00 1.95526544E-02-6.93149115E-06 1.10889183E-09-6.59584410E-14    2
 1.22822959E+04-1.67137903E+01 4.54746808E+00 4.63771460E-03 6.61340221E-05    3
-8.97456502E-08 3.61716165E-11 1.43843217E+04 7.30313471E+00 1.63702936E+04    4
iC4H8 Isobuten    T05/09C  4.H  8.   0.   0.G   200.000  6000.000 1000.       1
 8.94232121E+00 2.12900129E-02-7.61851464E-06 1.22641473E-09-7.32634442E-14    2
-6.67292929E+03-2.46775148E+01 3.30612340E+00 1.33377057E-02 5.65726066E-05    3
-8.46898088E-08 3.52403438E-11-4.04128388E+03 9.92304633E+00-2.11365432E+03    4
T2C4H8                  C   4H   80   00   0G   300.00   5000.00  1000.00     1
 0.82797676E+00 0.35864539E-01-0.16634498E-04 0.34732759E-08-0.26657398E-12    2
-0.30521033E+04 0.21342545E+02 0.12594252E+01 0.27808424E-01 0.87013932E-05    3
-0.24402205E-07 0.98977710E-11-0.29647742E+04 0.20501129E+02                   4
```

```
C5H10  2-Pentene  T06/10C  5.H 10.   0.   0.G   200.000  6000.000 1000.        1
 8.93261012E+00 2.89903124E-02-1.06341942E-05 1.73465637E-09-1.04436210E-13    2
-8.78335596E+03-1.73701098E+01 9.62243499E+00-2.31903373E-02 1.52217333E-04    3
-1.75855769E-07 6.61252866E-11-6.51503667E+03-8.74098747E+00-3.64832083E+03    4
iC4H9 isobutylrad T 6/04C  4.H  9.   0.   0.G   200.000  6000.000 1000.        1
 9.61250942E+00 2.28581786E-02-8.06391309E-06 1.28556553E-09-7.62730799E-14    2
 4.15218608E+03-2.66485099E+01 3.34476784E+00 2.31869650E-02 3.28261040E-05    3
-5.96398514E-08 2.58980820E-11 6.66201200E+03 9.68860372E+00 8.87422590E+03    4
nC4H9 n-butyl     T 7/04C  4.H  9.   0.   0.G   200.000  6000.000 1000.        1
 8.97401527E+00 2.39704154E-02-8.48703645E-06 1.35644127E-09-8.06234913E-14    2
 5.19161526E+03-2.31075609E+01 4.73737837E+00 9.69051565E-03 6.63846383E-05    3
-9.24799302E-08 3.74006099E-11 7.57382332E+03 4.91063455E+00 9.83838903E+03    4
sC4H9 s-butyl     T 6/04C  4.H  9.   0.   0.G   200.000  6000.000 1000.        1
 7.72287211E+00 2.43427284E-02-8.65476475E-06 1.38712529E-09-8.26084187E-14    2
 4.15004489E+03-1.43949625E+01 5.42089393E+00-9.12146870E-04 8.84998581E-05    3
-1.12115531E-07 4.38222782E-11 6.28927311E+03 5.04210029E+00 8.44598852E+03    4
tC4H9 t-butyl     T 6/04C  4.H  9.   0.   0.G   200.000  6000.000 1000.        1
 6.72557390E+00 2.53649194E-02-9.05306262E-06 1.45474620E-09-8.67934112E-14    2
 2.57430692E+03-8.89920414E+00 6.45910754E+00-1.02015930E-02 1.06310577E-04    3
-1.25717030E-07 4.75543216E-11 4.43420391E+03 1.30648608E+00 6.61981524E+03    4
nC4H10 n-butane   g12/00C  4.H 10.   0.   0.G   200.000  6000.000 1000.        1
 9.44547835E+00 2.57856620E-02-9.23613194E-06 1.48631762E-09-8.87891206E-14    2
-2.01383773E+04-2.63477585E+01 6.14474013E+00 1.64500242E-04 9.67848789E-05    3
-1.25486208E-07 4.97846257E-11-1.75989467E+04-1.08058878E+00-1.51289733E+04    4
C4H8O 2-Butanone  T09/10C  4.H  8.O  1.   0.G   200.000  6000.000 1000.        1
 9.29655016E+00 2.29172746E-02-8.22048591E-06 1.32404838E-09-7.91751980E-14    2
-3.34442311E+04-2.04993263E+01 6.61978185E+00 8.51847835E-03 5.10322077E-05    3
-6.58433042E-08 2.49110484E-11-3.15251691E+04-1.09485469E+00-2.88403536E+04    4
C4H9OO n-Butyl P  T04/09C  4.H  9.O  2.   0.G   200.000  6000.000 1000.        1
 1.23429985E+01 2.62571448E-02-9.56671199E-06 1.55186643E-09-9.30636032E-14    2
-1.38631285E+04-3.51216207E+01 7.72177591E+00-5.24480169E-03 1.23509561E-04    3
-1.57237681E-07 6.17433797E-11-1.05195922E+04-7.64797505E-01-7.64084185E+03    4
C4H9OOH   n-perox T03/09C  4.H 10.O  2.   0.G   200.000  6000.000 1000.        1
 1.28219158E+01 2.86823803E-02-1.02147914E-05 1.63572769E-09-9.73133952E-14    2
-3.07798233E+04-3.94377500E+01 8.00936535E+00-2.66942443E-04 1.16727305E-04    3
-1.51711952E-07 6.00701432E-11-2.75032149E+04-4.64152531E+00-2.43672606E+04    4
C4H8OOO2H    7/19/ 0 trmC   4H   9O   4    0G   300.000  5000.000 1387.000    61
 2.23244015e+01 2.05474775e-02-7.19076348e-06 1.13361536e-09-6.64744383e-14    2
-3.05468277e+04-8.32666070e+01 2.22400728e+00 7.04994620e-02-5.66978827e-05    3
 2.42627751e-08-4.29715459e-12-2.37391490e+04 2.38371533e+01                   4
C4H7O      6/26/95 thermC   4H   7O   1    0G   300.000  5000.000 1380.000    31
 1.30026331e+01 1.63104877e-02-5.57642899e-06 8.65670629e-10-5.02255667e-14    2
-1.25523385e+04-4.02608515e+01 2.67256826e+00 3.71198825e-02-2.06862859e-05    3
 5.48873888e-09-5.35864183e-13-8.58050888e+03 1.64848950e+01
C4H8O3     6/26/95 thermC   4H   8O   3    0G   300.000  5000.000 1396.000    51
 1.74383247e+01 2.16778876e-02-7.37772628e-06 1.14128811e-09-6.60391451e-14    2
-3.55892620e+04-5.71247140e+01 2.88497398e+00 5.63287929e-02-3.98403503e-05    3
 1.53891643e-08-2.51940787e-12-3.05246721e+04 2.09293355e+01                   4
C4H8OOH    7/19/ 0 thermC   4H   9O   2    0G   300.000  5000.000 1393.000    51
 1.58327906e+01 2.07220436e-02-7.09869028e-06 1.10302045e-09-6.40251984e-14    2
-8.53034314e+03-5.04399828e+01 1.51698234e+00 5.44584331e-02-3.84524319e-05    3
 1.48145523e-08-2.42809434e-12-3.49728423e+03 2.64916926e+01                   4
CH3O2      1/14/ 5 THERMC   1H   3O   2    0G   300.000  5000.000 1365.000    11
 6.34718801E+00 7.92089358E-03-2.76601913E-06 4.35360631E-10-2.54984762E-14    2
-1.83436055E+03-7.42552545E+00 3.80497590E+00 9.80784660E-03-3.90940624E-07    3
-2.23072602E-09 6.43310820E-13-4.55625796E+02 7.81789100E+00                   4
```

```
CH3O2H            T11/96C   1H   4O   2    0G   200.000  6000.000 1000.        1
 6.86907934E+00 1.00840883E-02-3.66515947E-06 5.96302681E-10-3.58894156E-14    2
-1.98402231E+04-1.24951986E+01 3.72654981E+00 7.51851847E-03 2.35970425E-05    3
-3.52694507E-08 1.42757614E-11-1.83982011E+04 6.52443362E+00-1.68074366E+04    4
C2H3OH     2/ 3/ 9 THERMC   2H   4O   1    0G   300.000  5000.000 1410.000    11
 8.32598158E+00 8.03387281E-03-2.63928405E-06 3.98410726E-10-2.26551155E-14    2
-1.83221436E+04-2.02080305E+01-1.27972260E-01 3.38506073E-02-3.30644935E-05    3
 1.64858739E-08-3.19935455E-12-1.59914544E+04 2.30438601E+01                   4
CH2CH2O2H  28/05/14     C   2H   5O   2    0g   300.000  5000.000 1000.00     31
 0.26749417E+02-0.30386297E-01 0.28740447E-04-0.96311094E-08 0.10906622E-11    2
-0.49379551E+04-0.12098509E+03-0.14475424E+01 0.57893153E-01-0.98292957E-04    3
 0.90537153E-07-0.32061134E-10 0.30520405E+04 0.23928379E+02 0.44876113E+04    4
O2C2H4OH   28/05/14     C   2H   5O   3    0g   300.000  5000.000 1000.00     31
-0.16543036E+01 0.38781536E-01-0.22486212E-04 0.59488557E-08-0.58576779E-12    2
-0.26643532E+05 0.38195078E+02 0.36884512E+01 0.18769900E-01 0.24416568E-04    3
-0.49201620E-07 0.22315538E-10-0.28407371E+05 0.10507046E+02-0.26345923E+05    4
C2H4O2OH   28/05/14     C   2H   5O   3    0g   300.000  5000.000 1000.00     31
 0.79197195E+01 0.19990160E-01-0.95442023E-05 0.21985525E-08-0.19567624E-12    2
-0.29103619E+05-0.11056179E+02 0.20569303E+01 0.31673374E-01-0.63375673E-05    3
-0.16996096E-07 0.99692830E-11-0.27385645E+05 0.20012978E+02-0.25451046E+05    4
NE REF ELEMENT    L10/90NE  100  0    0    0G   200.000  6000.000 1000.        1
 0.25000000E 01 0.00000000E 00 0.00000000E 00 0.00000000E 00 0.00000000E 00    2
-0.74537500E 03 0.33553227E 01 0.25000000E 01 0.00000000E 00 0.00000000E 00    3
 0.00000000E 00-0.74537498E 03 0.33553227E 01 0.00000000E 00 0.00000000E+00    4
nC5H12     1/14/95 thermC   5H  12    0    0g   300.000  5000.000 1390.000    41
 1.57257603e+01 2.61086045e-02-8.90970996e-06 1.38102248e-09-8.00296536e-14    2
-2.60519543e+04-6.03365457e+01-7.36766119e-01 6.07200973e-02-3.57592761e-05    3
 1.04907041e-08-1.21487315e-12-1.98934934e+04 2.95358286e+01                   4
iC5H11 neopentyl  T03/97C   5H  11    0    0G   298.150  5000.000 1000.        1
 2.60303371E+01-3.89073388E-03 1.18835338E-05-2.05929731E-09 1.06754076E-13    2
-5.66523187E+03-1.12796509E+02-4.46503561E+00 9.32367831E-02-1.41121240E-04    3
 1.52613544E-07-6.83999414E-11 2.30110241E+03 4.28019931E+01 4.13644099E+03    4
iC5H10 2MB-2-ene  T11/10C  5.H 10.   0.   0.G   200.000  6000.000 1000.        1
 8.68767295E+00 2.88066020E-02-1.02545416E-05 1.64495843E-09-9.80249125E-14    2
-9.66135150E+03-1.94356921E+01 8.57165202E+00-1.08173231E-02 1.16249570E-04    3
-1.36476697E-07 5.12594651E-11-7.64248930E+03-9.06119919E+00-4.78609371E+03    4
C5H9 2-en-1-yl    A 4/05C  5.H  9.   0.   0.G   200.000  6000.000 1000.        1
 1.11277742E+01 2.38252436E-02-8.44023460E-06 1.34549364E-09-7.97578298E-14    2
 8.68711411E+03-3.07833429E+01 2.34425040E+00 3.21504141E-02 2.45295981E-05    3
-5.81110933E-08 2.68653496E-11 1.17932336E+04 1.81635883E+01 1.40357192E+04    4
C5H8 2-Pentyne    T10/15C  5.H  8.   0.   0.G   200.000  5000.000 1000.        1
 1.00381240E+01 2.38209300E-02-9.10187613E-06 1.61975738E-09-1.09252936E-13    2
 1.03544726E+04-2.64618273E+01 5.25398553E+00 1.20844047E-02 5.63009183E-05    3
-7.90280096E-08 3.15136172E-11 1.30433100E+04 4.59783012E+00 1.55030182E+04    4
C5H9O               thrmC   5H   9O   1    0g   300.000  5000.000 1381.000     1
 1.58052948e+01 2.12787457e-02-7.31842496e-06 1.14049355e-09-6.63446381e-14    2
-1.42827587e+04-5.34016678e+01 2.00033269e+00 4.96074565e-02-2.87470600e-05    3
 8.26666830e-09-9.51074212e-13-9.01010845e+03 2.22761791e+01                   4
C5H10CHO  4/9/14        C   6H  11O   1    0G   300.00  3000.000  1000.0       1
 0.10703713E+02 0.38487167E-01-0.17369552E-04 0.38363865E-08-0.33089043E-12    2
-0.11401732E+05-0.32273335E+02 0.10390741E+01 0.71096548E-01-0.63571553E-04    3
 0.37750759E-07-0.10990906E-10-0.89877065E+04 0.16339461E+02-0.60127496E+04    4
C6H10 1-Hexayne   T02/15C  6.H 10.   0.   0.G   200.000  6000.000 1000.        1
 1.25920263E+01 2.80388372E-02-1.00900599E-05 1.62462801E-09-9.69272153E-14    2
 8.60224566E+03-3.73619548E+01 3.70967957E+00 3.30843519E-02 3.21846406E-05    3
-6.65353226E-08 2.96251550E-11 1.19658395E+04 1.31017210E+01 1.47092252E+04    4
```

```
C6H11  2-ene-6-yl A07/05C  6.H 11.   0.   0.G   200.000  6000.000 1000.        1
 1.27605793E+01 3.01168355E-02-1.08197236E-05 1.73977051E-09-1.03692791E-13    2
 1.22100274E+04-3.54020393E+01 6.23788522E+00 1.86370994E-02 7.02342856E-05    3
-1.04621010E-07 4.32055091E-11 1.53829414E+04 5.23415999E+00 1.85052897E+04    4
iC6H12 2Me-2en    T10/10C  6.H 12.   0.   0.G   200.000  6000.000 1000.        1
 1.07253352E+01 3.46133915E-02-1.23985588E-05 1.99405975E-09-1.18968236E-13    2
-1.32194553E+04-2.81050813E+01 8.96524961E+00-7.30015904E-03 1.33400236E-04    3
-1.62499260E-07 6.22491935E-11-1.04524950E+04-7.69362144E+00-7.21713342E+03    4
iC6H11                  C   6H  11          G   250.000  5000.000   995.043    1
 1.29348867E+01 3.00041589E-02-1.06357956E-05 1.70838534E-09-1.02222245E-13    2
 1.01296981E+04-3.80331109E+01 3.48968205E+00 3.57445901E-02 2.92944128E-05    3
-5.75949016E-08 2.29756337E-11 1.36048682E+04 1.55048140E+01                   4
C6H12CHO    3/4/96 thermC   7H  13O   1    0g   300.000  5000.000 1395.000    1
 2.42514472e+01 2.84438313e-02-9.77077660e-06 1.52152073e-09-8.84667232e-14    2
-2.15083432e+04-9.95417905e+01-1.27560491e+00 8.80197598e-02-6.28266939e-05    3
 2.29973864e-08-3.42459126e-12-1.26633185e+04 3.75312437e+01                   4
cyC6H9O    3/17/ 6 thermC   6H   9O   1    0g   300.000  5000.000 1369.000   11
-0.74704407E+01 0.74757622E-01-0.41387678E-04 0.10473466E-07-0.99677029E-12    2
 0.60398853E+04 0.59505359E+02-0.23187144E+01 0.50151874E-01 0.34652255E-04    3
-0.86353641E-07 0.39225621E-10 0.40066875E+04 0.32724381E+02 0.56964157E+04    4
C7H16 n-heptane   P10/85C  7.H 16.   0.   0.G   200.000  6000.000 1000.        1
 2.04565203E+01 3.48575357E-02-1.09226846E-05 1.67201776E-09-9.81024850E-14    2
-3.25556365E+04-8.04405017E+01 1.11532994E+01-9.49419773E-03 1.95572075E-04    3
-2.49753662E-07 9.84877715E-11-2.67688904E+04-1.59096837E+01-2.25846141E+04    4
C7H15 n-heptyl-1  T 4/16C  7.H 15.   0.   0.G   200.000  6000.000 1000.        1
 1.62820751E+01 4.05171647E-02-1.47864421E-05 2.41764634E-09-1.45776873E-13    2
-6.07971812E+03-5.42045176E+01 1.02804136E+01 7.01553566E-04 1.59551347E-04    3
-2.09593179E-07 8.33445318E-11-1.97820286E+03-1.03020940E+01 2.15286289E+03    4
C7H15O2                 C   7H  15O   2    0G   300.000  5000.000 1390.000   71
 2.60535640e+01 3.43831688e-02-1.18713247e-05 1.85450241e-09-1.08052399e-13    2
-3.06842095e+04-1.05407563e+02 3.55252917e-01 9.42381007e-02-6.66955106e-05    3
 2.54795583e-08-4.13211105e-12-2.15795254e+04 3.29433435e+01                   4
C7H14O3    7/19/ 0 thermC   7H  14O   3    0g   300.000  5000.000 1387.000   81
 2.88330388e+01 3.20168096e-02-1.11508456e-05 1.75226159e-09-1.02520451e-13    2
-6.20142474e+04-1.17499704e+02 1.52936692e+00 9.58173466e-02-6.96688520e-05    3
 2.69540382e-08-4.38728126e-12-5.23839542e+04 2.93851334e+01                   4
iC7H15 NEOPENTYL-2T09/06C   7H  15    0    0G   200.000  6000.000 1000.        1
 1.54723688E+01 3.98401859E-02-1.42645004E-05 2.29168756E-09-1.36572491E-13    2
-8.04601795E+03-5.08362222E+01 6.14236886E+00 4.31168500E-02 3.15175070E-05    3
-6.58680014E-08 2.82944448E-11-4.26130046E+03 3.05760810E+00-3.51899390E+02    4
C7H13O                  C   7H  13O   1    0G   250.000  5000.000  1000.000    1
 0.31968961E+01 0.64634774E-01-0.31915558E-04 0.75118058E-08-0.68060720E-12    2
-0.16045544E+05 0.21466624E+02-0.25535909E+01 0.10974389E+00-0.13700611E-03    3
 0.11044552E-06-0.37893748E-10-0.16110233E+05 0.43617783E+02-0.13006976E+05    4
iC8H15     7/20/ 0 thermC   8H  15    0    0g   300.000  5000.000 1397.000   51
 2.60931337e+01 3.17629740e-02-1.07800358e-05 1.66534077e-09-9.62985504e-14    2
-8.00312155e+03-1.15651475e+02-3.74987946e+00 1.05476476e-01-8.12781961e-05    3
 3.26271703e-08-5.33783606e-12 1.92249518e+03 4.31416185e+01                   4
iC8H17 2,3,3-TMP  T 4/16C  8.H 17.   0.   0.G   200.000  6000.000 1000.        1
 1.81425745E+01 4.56235008E-02-1.61606216E-05 2.58366581E-09-1.53601024E-13    2
-1.15362605E+04-7.08181467E+01 3.81040750E+00 6.14767143E-02 2.28430253E-05    3
-7.07276491E-08 3.26330205E-11-6.36141148E+03 9.07036826E+00-2.41544000E+03    4
aC8H17     7/27/95 THERMC   8H  17    0    0G   300.000  5000.000 1396.00      1
 2.67069782e+01 3.57660601e-02-1.22178704e-05 1.89536630e-09-1.09907843e-13    2
-1.57229692e+04-1.17001113e+02-3.41944741e+00 1.06803189e-01-7.65411563e-05    3
 2.85341682e-08-4.36478649e-12-5.33514196e+03 4.45471727e+01                   4
```

```
bC8H17     7/27/95 THERMC   8H  17    0    0G   300.000  5000.000 1393.00      1
 2.64569179e+01 3.55420752e-02-1.20520984e-05 1.86089357e-09-1.07571894e-13    2
-1.70392791e+04-1.16245511e+02-3.09104262e+00 1.02318896e-01-6.84858873e-05    3
 2.30183940e-08-3.07013080e-12-6.62829069e+03 4.31173932e+01                   4
cC8H17     7/27/95 THERMC   8H  17    0    0G   300.000  5000.000 1390.00      1
 2.51497158e+01 3.71096845e-02-1.26854483e-05 1.96873429e-09-1.14193894e-13    2
-1.83768332e+04-1.09056834e+02-9.73159697e-02 8.92653724e-02-5.12873814e-05    3
 1.37640528e-08-1.27788396e-12-8.91212728e+03 2.89791898e+01                   4
dC8H17     7/27/95 THERMC   8H  17    0    0G   300.000  5000.000 1396.00      1
 2.67069782e+01 3.57660601e-02-1.22178704e-05 1.89536630e-09-1.09907843e-13    2
-1.61255862e+04-1.18098245e+02-3.41944741e+00 1.06803189e-01-7.65411563e-05    3
 2.85341682e-08-4.36478649e-12-5.73775897e+03 4.34500414e+01                   4
C8H16  1-octene    n 4/87C   8H  16    0    0G   200.000  6000.000 1000.000     1
 2.43378771E+01 3.22574569E-02-1.03389736E-05 1.65359772E-09-1.00909018E-13    2
-2.14383953E+04-9.82405127E+01 1.01483726E+01 1.25438065E-03 1.85245518E-04    3
-2.49087148E-07 1.00247926E-10-1.43267638E+04-8.51901783E+00-1.00535089E+04    4
nC8H15 1-octenyl- T 3/00C   8H  15    0    0G   298.150  5000.000 1000.        1
 1.86031870E+01 4.07347321E-02-1.52146579E-05 2.66612666E-09-1.77710586E-13    2
 3.77573497E+03-6.42994408E+01 3.96580128E+00 5.00731521E-02 4.58633610E-05    3
-9.55246040E-08 4.20968508E-11 9.47734142E+03 1.90962113E+01 1.31216392E+04    4
cC8H17OO    7/20/ 0 thrmC   8H  17O   2    0g   300.000  5000.000 1394.000    91
 3.22733666e+01 3.60035914e-02-1.24584643e-05 1.94942256e-09-1.13722419e-13    2
-2.80443391e+04-1.40571052e+02-1.84900727e+00 1.18470376e-01-8.99609127e-05    3
 3.56283674e-08-5.79743151e-12-1.64331259e+04 4.17717295e+01                   4
C8H16O3    7/20/ 0 thermC   8H  16O   3    0g   300.000  5000.000 1394.000    91
 3.50696425e+01 3.40096645e-02-1.18587999e-05 1.86530452e-09-1.09217949e-13    2
-6.88169429e+04-1.58744646e+02-3.14440571e+00 1.26997795e-01-9.92838921e-05    3
 3.96018910e-08-6.39794193e-12-5.59585699e+04 4.51031280e+01                   4
C7H15O 3,3-dimet  T10/99C   7H  15O   1    0G   298.150  5000.000 1000.        1
 2.09858953E+01 3.85709050E-02-1.46086654E-05 2.59555359E-09-1.75052645E-13    2
-2.75558714E+04-9.67484012E+01 1.76386765E-01 7.26245771E-02 2.14651033E-07    3
-5.23551849E-08 2.64458952E-11-2.03008094E+04 1.71949368E+01-1.71093666E+04    4
C7H15O4                  C   7H  15O   4    0G   300.000  5000.000 1390.000     1
 3.28358296e+01 3.32767285e-02-1.15833285e-05 1.81958638e-09-1.06434419e-13    2
-4.52873003e+04-1.35975710e+02 1.40912479e+00 1.10720834e-01-8.71178075e-05    3
 3.63662749e-08-6.28350689e-12-3.46304788e+04 3.16223383e+01                   4
aC7H14                   C   7H  14    0    0G   200.000  6000.000 1000.        1
 2.00329343E+01 3.01875580E-02-9.96912897E-06 1.59376458E-09-9.64314031E-14    2
-1.70512608E+04-7.66778730E+01 8.70539860E+00 2.80074488E-03 1.55206000E-04    3
-2.09014025E-07 8.40505778E-11-1.12661494E+04-4.46493550E+00-7.54824999E+03    4
cC7H14     2/ 4/95 THERMC   7H  14    0    0G   300.000  5000.000 1395.00      1
 2.24887015e+01 2.96738400e-02-1.00479879e-05 1.54993215e-09-8.95338318e-14    2
-2.23998822e+04-9.74445306e+01-3.31532000e+00 9.05539714e-02-6.48360116e-05    3
 2.39274057e-08-3.58919418e-12-1.35509173e+04 4.08389011e+01                   4
aC7H14OO                 C   7H  14O   2    0G   300.000  3000.000              1
 0.29110431E+02 0.22295298E-01-0.36406130E-05-0.16383943E-09 0.63481908E-13    2
-0.41037976E+05-0.13280678E+03-0.40188478E+01 0.12364137E+00-0.13723807E-03    3
 0.96367411E-07-0.30556074E-10-0.32058151E+05 0.36972627E+02-0.28800818E+02    4
bC7H14OO                 C   7H  14O   2    0G   300.000  3000.000              1
 0.29110431E+02 0.22295298E-01-0.36406130E-05-0.16383943E-09 0.63481908E-13    2
-0.41037976E+05-0.13280678E+03-0.40188478E+01 0.12364137E+00-0.13723807E-03    3
 0.96367411E-07-0.30556074E-10-0.32058151E+05 0.36972627E+02-0.28800818E+02    4
cC7H14OO                 C   7H  14O   2    0G   300.000  3000.000              1
 0.29110431E+02 0.22295298E-01-0.36406130E-05-0.16383943E-09 0.63481908E-13    2
-0.41037976E+05-0.13280678E+03-0.40188478E+01 0.12364137E+00-0.13723807E-03    3
 0.96367411E-07-0.30556074E-10-0.32058151E+05 0.36972627E+02-0.28800818E+02    4
```

```
C7H13 1-hepten4-ylT 3/00C  7.H 13.   0.   0.G   298.150  5000.000 1000.        1
 1.60018015E+01 3.54427457E-02-1.32165151E-05 2.31246011E-09-1.53963769E-13    2
 7.55716567E+03-4.44583440E+01 3.79165044E+00 4.06710071E-02 4.73501574E-05    3
-9.16895795E-08 4.01452434E-11 1.24049636E+04 2.56340050E+01 1.55992356E+04    4
nC6H14     7/19/ 0 thermC   6H  14    0    0g   300.000  5000.000 1397.000    51
 2.06883286e+01 2.88781796e-02-9.81789236e-06 1.51824834e-09-8.78482687e-14    2
-3.33494682e+04-8.99844746e+01-3.12747832e+00 8.44727715e-02-5.93030427e-05    3
 2.15157398e-08-3.18466066e-12-2.51021282e+04 3.78888101e+01                   4
iC6H13  2MP-1YL   T11/95C   6H  13    0    0G   298.150  5000.000 1000.        1
 0.14754628E+02 0.33919022E-01-0.12689277E-04 0.22271946E-08-0.14866840E-12    2
-0.39802078E+04-0.49287611E+02 0.47593240E+01 0.25922476E-01 0.79813586E-04    3
-0.12504262E-06 0.52491365E-10 0.46852943E+03 0.10765884E+02 0.35225167E+04    4
aC6H12 1-Hexene   T10/10C  6.H 12.   0.   0.G   200.000  6000.000 1000.        1
 1.22080929E+01 3.32790650E-02-1.19875911E-05 1.92939941E-09-1.15062647E-13    2
-1.12223522E+04-3.43171769E+01 6.59375238E+00 5.81209593E-03 1.17056541E-04    3
-1.57671202E-07 6.35227163E-11-7.71664325E+03 4.70097229E+00-4.73979778E+03    4
C5H11 n-Pentyl    T 6/13C  5.H 11.   0.   0.G   200.000  6000.000 1000.        1
 1.08124578E+01 2.94760248E-02-1.05284277E-05 1.69017240E-09-1.00707534E-13    2
 1.68606610E+03-2.84779199E+01 6.03926263E+00 9.27666049E-03 8.73715863E-05    3
-1.19342212E-07 4.80042218E-11 4.56271549E+03 4.06139688E+00 7.33438290E+03    4
C4H8O             T 5/92C   4H   8O   1    0G   300.000  5000.000 1371.000    51
 1.54227092e+01 1.70211052e-02-6.06347951e-06 9.67354762e-10-5.71992419e-14    2
-2.20194174e+04-6.13871862e+01-2.53690104e+00 5.43995707e-02-3.43390305e-05    3
 1.01079922e-08-1.10262736e-12-1.52980680e+04 3.67400719e+01                   4
C4H8O2 DIOXANE    T03/97C   4H   8O   2    0G   200.000  6000.000 1000.        1
 1.09080022E+01 2.65730193E-02-9.70934955E-06 1.58519471E-09-9.56379521E-14    2
-4.38420203E+04-3.79862937E+01 3.64975602E+00 3.21199783E-03 1.12973931E-04    3
-1.50581748E-07 6.00072918E-11-3.97765405E+04 9.86785750E+00-3.78167324E+04    4
C7H15OO                C   7H  15O   2    0G   300.000  5000.000 1389.000    81
 2.74034778e+01 3.27527893e-02-1.12991770e-05 1.76444649e-09-1.02786945e-13    2
-2.48636651e+04-1.10201978e+02 8.49786005e-01 9.25107196e-02-6.25359834e-05    3
 2.17880390e-08-3.12720398e-12-1.53640679e+04 3.32997487e+01                   4
C6H12OO                C   6H  12O   2    0G   300.000  3000.000              1
 0.25983015E+02 0.18693236E-01-0.30525996E-05-0.13730236E-09 0.53217927E-13    2
-0.37243285E+05-0.11801170E+03-0.43396048E+01 0.11557322E+00-0.13981874E-03    3
 0.10522597E-06-0.34655254E-10-0.29171069E+05 0.36508646E+02-0.26374789E+02    4
iC8H18 isooctane  P 4/85C  8.H 18.   0.   0.G   200.000  6000.000 1000.        1
 1.76160941E+01 5.13323108E-02-1.65307266E-05 2.43232275E-09-1.35572757E-13    2
-3.63461118E+04-6.86446285E+01 8.15741071E-01 7.32647307E-02 1.78301503E-05    3
-6.93592790E-08 3.21630852E-11-3.04774255E+04 2.41511097E+01-2.69420567E+04    4
iC8H16     7/20/ 0 thermC   8H  16    0    0g   300.000  5000.000 1394.000    61
 2.56756746e+01 3.41801998e-02-1.16002952e-05 1.79195478e-09-1.03613002e-13    2
-2.62458324e+04-1.13928273e+02-2.79610447e+00 1.00836172e-01-7.12250651e-05    3
 2.60659824e-08-3.90031814e-12-1.64002496e+04 3.88854068e+01                   4
C8H17 n-octyl-1   T 3/16C  8.H 17.   0.   0.G   200.000  6000.000 1000.        1
 1.86449550E+01 4.61977765E-02-1.68984153E-05 2.76915624E-09-1.67267495E-13    2
-9.73086339E+03-6.50889980E+01 1.18082518E+01-8.50348136E-04 1.87697700E-04    3
-2.45690702E-07 9.75813027E-11-5.00355266E+03-1.47298487E+01-3.01881891E+02    4
aC8H17O4      7/20/ 0 tmC   8H  17O   4    0g   300.000  5000.000 1391.000    91
 3.60794609e+01 3.77494166e-02-1.31295433e-05 2.06141539e-09-1.20538637e-13    2
-4.68142419e+04-1.56529322e+02-5.13569052e-01 1.27497436e-01-9.96783958e-05    3
 4.09976757e-08-6.95279847e-12-3.44189277e+04 3.86776062e+01                   4
bC8H17O4      7/20/ 0 tmC   8H  17O   4    0g   300.000  5000.000 1393.000    91
 3.75785800e+01 3.64513715e-02-1.26763216e-05 1.99010404e-09-1.16363556e-13    2
-5.25653329e+04-1.68169424e+02-1.49381512e+00 1.36761538e-01-1.14348621e-04    3
 4.99098535e-08-8.85373352e-12-3.97954365e+04 3.86453145e+01                   4
```

```
cC8H17O4      7/20/ 0 tmC   8H  17O   4    0g   300.000  5000.000 1393.000    91
 3.75785800e+01 3.64513715e-02-1.26763216e-05 1.99010404e-09-1.16363556e-13    2
-5.25653329e+04-1.68169424e+02-1.49381512e+00 1.36761538e-01-1.14348621e-04    3
 4.99098535e-08-8.85373352e-12-3.97954365e+04 3.86453145e+01                    4
aC8H17OO    7/20/ 0 thrmC   8H  17O   2    0g   300.000  5000.000 1394.000    91
 3.22733666e+01 3.60035914e-02-1.24584643e-05 1.94942256e-09-1.13722419e-13    2
-2.80443391e+04-1.40571052e+02-1.84900727e+00 1.18470376e-01-8.99609127e-05    3
 3.56283674e-08-5.79743151e-12-1.64331259e+04 4.17717295e+01                    4
bC8H17OO    7/20/ 0 thrmC   8H  17O   2    0g   300.000  5000.000 1394.000    91
 3.22733666e+01 3.60035914e-02-1.24584643e-05 1.94942256e-09-1.13722419e-13    2
-2.80443391e+04-1.40571052e+02-1.84900727e+00 1.18470376e-01-8.99609127e-05    3
 3.56283674e-08-5.79743151e-12-1.64331259e+04 4.17717295e+01                    4
cC8H17OO    7/20/ 0 thrmC   8H  17O   2    0g   300.000  5000.000 1394.000    91
 3.22733666e+01 3.60035914e-02-1.24584643e-05 1.94942256e-09-1.13722419e-13    2
-2.80443391e+04-1.40571052e+02-1.84900727e+00 1.18470376e-01-8.99609127e-05    3
 3.56283674e-08-5.79743151e-12-1.64331259e+04 4.17717295e+01                    4
aC8H17O2   7/20/ 0 thermC   8H  17O   2    0g   300.000  5000.000 1393.000    81
 3.02815958e+01 3.78729072e-02-1.30468383e-05 2.03524213e-09-1.18471267e-13    2
-3.48032462e+04-1.31647036e+02-1.78614072e+00 1.14754903e-01-8.50604719e-05    3
 3.34040935e-08-5.45173228e-12-2.37742056e+04 4.00275514e+01                    4
bC8H17O2   7/20/ 0 thermC   8H  17O   2    0g   300.000  5000.000 1394.000    81
 3.09351615e+01 3.74102564e-02-1.29070970e-05 2.01544850e-09-1.17398911e-13    2
-3.77457753e+04-1.36730800e+02-3.07002356e+00 1.22640438e-01-9.72202764e-05    3
 4.09127625e-08-7.09102547e-12-2.64014308e+04 4.40345691e+01                    4
cC8H17O2   7/20/ 0 thermC   8H  17O   2    0g   300.000  5000.000 1394.000    81
 3.09721695e+01 3.73366082e-02-1.28724179e-05 2.00907464e-09-1.16989072e-13    2
-3.79648855e+04-1.38456446e+02-1.80143766e+00 1.18030511e-01-9.10630966e-05    3
 3.73480361e-08-6.33999307e-12-2.68892049e+04 3.62716425e+01                    4
dC8H17O2   7/20/ 0 thermC   8H  17O   2    0g   300.000  5000.000 1393.000    81
 3.02815958e+01 3.78729072e-02-1.30468383e-05 2.03524213e-09-1.18471267e-13    2
-3.48032462e+04-1.32744167e+02-1.78614072e+00 1.14754903e-01-8.50604719e-05    3
 3.34040935e-08-5.45173228e-12-2.37742056e+04 3.89304200e+01                    4
C6H13      1/ 2/ 7 THERMC   6H  13    0    0G   300.000  5000.000 1380.000    51
 1.83687363E+01 2.80268110E-02-9.47032396E-06 1.45888527E-09-8.42002461E-14    2
-6.46093974E+03-6.90934018E+01 2.29560149E-01 6.33327323E-02-3.24135431E-05    3
 6.46387687E-09-9.61420427E-14 5.25639156E+02 3.08006138E+01                    4
N-C10H22 DECANE   T 5/99C  10H  22    0    0G   200.000  6000.000 1000.         1
 2.94782956E+01 4.90518943E-02-1.70317179E-05 2.72919300E-09-1.63370772E-13    2
-4.43022624E+04-1.24062121E+02 1.54328173E+01-1.32979232E-02 2.82480581E-04    3
-3.65923298E-07 1.45372117E-10-3.58632831E+04-2.79454341E+01-3.00118419E+04    4
aC10H21  1-decyl  T 3/16C 10.H 21.   0.   0.G   200.000  6000.000 1000.         1
 2.33758749E+01 5.75359680E-02-2.10967257E-05 3.46308793E-09-2.09433499E-13    2
-1.70891847E+04-8.68821108E+01 1.48509982E+01-3.85329086E-03 2.43709387E-04    3
-3.17546124E-07 1.25907801E-10-1.11095267E+04-2.35343842E+01-5.26789913E+03    4
bC10H21 n-Decyl-2 T 4/16C 10.H 21.   0.   0.G   200.000  6000.000 1000.         1
 2.02819691E+01 6.04932528E-02-2.17509386E-05 3.50236435E-09-2.09067061E-13    2
-1.82125216E+04-7.54873889E+01 1.21565346E+01 4.71773061E-03 2.10335561E-04    3
-2.71092255E-07 1.06200010E-10-1.21946529E+04-1.46973325E+01-6.98778401E+03    4
C10H20 2-Decene   T 8/14C 10.H 20.   0.   0.G   200.000  6000.000 1000.         1
 1.82009818E+01 5.97763928E-02-2.16078885E-05 3.49412274E-09-2.09204047E-13    2
-2.69739853E+04-6.43937960E+01 1.44527752E+01-2.21660015E-02 2.66198188E-04    3
-3.22280255E-07 1.23449698E-10-2.14781263E+04-2.27860118E+01-1.63810014E+04    4
C9H19      1/ 2/ 7 THERMC   9H  19    0    0G   300.000  5000.000 1390.000    81
 2.83097514E+01 4.12657344E-02-1.40383289E-05 2.17174871E-09-1.25692307E-13    2
-1.74516030E+04-1.16837897E+02-1.04387292E+00 1.05617283E-01-6.68199971E-05    3
 2.14486166E-08-2.77404275E-12-6.80818512E+03 4.23518992E+01                    4
```

```
C9H18      1/ 2/ 7 THERMC   9H  18    0    0G   300.000  5000.000 1392.000    71
 2.76142176E+01 3.96825287E-02-1.34819446E-05 2.08390452E-09-1.20539294E-13    2
-2.65709061E+04-1.16618623E+02-2.16108263E+00 1.06958297E-01-7.10973244E-05    3
 2.43971077E-08-3.42771547E-12-1.59890847E+04 4.41245128E+01                   4
C10H21O2          Date  H  21O   2C  10     G   300.000  3000.000  1000.000    1
 2.84782000E+01 5.37539000E-02-1.68186000E-05 2.51367000E-09-1.47208000E-13    2
-3.74118000E+04-1.09121000E+02 5.31404000E+00 8.93873000E-02 1.45351000E-05    3
-7.49250000E-08 3.35325000E-11-2.98918000E+04 1.69741000E+01                   4
C10H20OOH         Date  H  21O   2C  10     G   300.000  3000.000  1000.000    1
 2.92019000E+01 5.15917000E-02-1.57327000E-05 2.30306000E-09-1.32640000E-13    2
-3.11192000E+04-1.08855000E+02 5.15231000E+00 9.97913000E-02-1.80635000E-05    3
-4.18435000E-08 2.22786000E-11-2.38380000E+04 1.93526000E+01                   4
O2C10H20OOH       Date  H  21O   4C  10     G   300.000  3000.000  1000.000    1
 3.50907000E+01 5.10590000E-02-1.54345000E-05 2.24627000E-09-1.28901000E-13    2
-5.12675000E+04-1.37750000E+02 4.81972000E-01 1.45020000E-01-9.99308000E-05    3
 2.60422000E-08 1.19358000E-12-4.16875000E+04 4.13429000E+01                   4
OC10H20OOH        Date  H  20O   3C  10     G   300.000  3000.000  1000.000    1
 2.36731000E+01 6.16392000E-02-2.09836000E-05 3.33166000E-09-2.03590000E-13    2
-7.18258000E+04-7.77662000E+01 8.80733000E+00 6.50623000E-02 6.95058000E-05    3
-1.26905000E-07 5.10991000E-11-6.65361000E+04 6.84155000E+00                   4
N-C12H26          T 5/99C  12H  26    0    0G   200.000  6000.000 1000.       1
 3.70187925E+01 5.54721488E-02-1.92079548E-05 3.08175574E-09-1.84800617E-13    2
-5.26984458E+04-1.61453501E+02 2.13264480E+01-3.86394002E-02 3.99476113E-04    3
-5.06681097E-07 2.00697878E-10-4.22475053E+04-4.85848300E+01-3.49836226E+04    4
aC12H25    1/ 2/ 7 THERMC  12H  25    0    0G   300.000  5000.000 1390.000    11
 3.80921885E+01 5.42107848E-02-1.84205517E-05 2.84762173E-09-1.64731748E-13    2
-2.98194375E+04-1.66882734E+02-1.85028741E+00 1.42670708E-01-9.18916555E-05    3
 3.00883392E-08-3.97454300E-12-1.54530435E+04 4.93702421E+01                   4
bC12H25    1/ 2/ 7 THERMC  12H  25    0    0G   300.000  5000.000 1385.000    11
 3.79688268E+01 5.38719464E-02-1.82171263E-05 2.80774503E-09-1.62108420E-13    2
-3.12144988E+04-1.65805933E+02-1.36787089E+00 1.37355348E-01-8.24076158E-05    3
 2.36421562E-08-2.47435932E-12-1.67660539E+04 4.83521895E+01                   4
C12H24     1/22/ 7 THERMC  12H  24    0    0G   300.000  5000.000 1391.000    11
 3.74002111E+01 5.26230753E-02-1.78624319E-05 2.75949863E-09-1.59562499E-13    2
-3.89405962E+04-1.64892663E+02-2.96342681E+00 1.43992360E-01-9.61384015E-05    3
 3.30174473E-08-4.62398190E-12-2.46345299E+04 5.29158870E+01                   4
C12H23     1/22/ 7 THERMC  12H  23    0    0G   300.000  5000.000 1391.000    11
 3.71516071E+01 5.09574750E-02-1.74320046E-05 2.70698624E-09-1.57088382E-13    2
-2.19833461E+04-1.64992468E+02-3.04897817E+00 1.41284540E-01-9.41858477E-05    3
 3.21335288E-08-4.46649750E-12-7.64465960E+03 5.22139103E+01                   4
C12H25O2   7/23/ 7 THERMC  12H  25O   2    0G   300.000  5000.000 1389.000    21
 4.10720559E+01 5.76223879E-02-1.98682057E-05 3.10098353E-09-1.80567383E-13    2
-4.84961160E+04-1.77176648E+02 4.13301762E-01 1.47893311E-01-9.69755376E-05    3
 3.35724323E-08-4.91454646E-12-3.36844450E+04 4.32258761E+01                   4
C12H24OOH  7/23/ 7 THERMC  12H  25O   2    0G   300.000  5000.000 1387.000    31
 4.29994696E+01 5.50833554E-02-1.88955870E-05 2.93978363E-09-1.70823564E-13    2
-4.30658136E+04-1.85856878E+02 1.60721186E-01 1.49325879E-01-9.67266789E-05    3
 3.17154092E-08-4.20449417E-12-2.75569298E+04 4.63656051E+01                   4
O2C12H24OOH 7/23/7 THERMC  12H  25O   4    0G   300.000  5000.000 1389.000    41
 4.78237378E+01 5.66012764E-02-1.96226767E-05 3.07404604E-09-1.79468346E-13    2
-6.30929400E+04-2.07768890E+02 6.91692611E-01 1.67000994E-01-1.20729787E-04    3
 4.63412670E-08-7.45842745E-12-4.65446291E+04 4.56074372E+01                   4
HO2C12H23OOH       THERMC  12H  25O   4    0G   300.000  5000.000 1389.000    41
 4.78237378E+01 5.66012764E-02-1.96226767E-05 3.07404604E-09-1.79468346E-13    2
-6.30929400E+04-2.07768890E+02 6.91692611E-01 1.67000994E-01-1.20729787E-04    3
 4.63412670E-08-7.45842745E-12-4.65446291E+04 4.56074372E+01                   4
```

```
OC12H23O2H 7/23/ 7 THERMC  12H  24O   3    0G   300.000  5000.000 1390.000    31
 4.58270142E+01 5.36021643E-02-1.85842108E-05 2.91164544E-09-1.70003340E-13    2
-7.84952427E+04-2.01938484E+02-8.15246773E-01 1.61762409E-01-1.15472154E-04    3
 4.29870811E-08-6.63426907E-12-6.21080428E+04 4.90271786E+01                   4
OC12H23O          T 5/09C 12.H 23.O  2.   0.G   298.150  5000.000 1000.       1
 3.08789431E+01 6.68262235E-02-2.48456449E-05 4.33699615E-09-2.88543169E-13    2
-5.73922228E+04-1.19862468E+02-2.12963756E+00 1.62421300E-01-1.41506204E-04    3
 7.76995449E-08-1.99735443E-11-4.76979641E+04 5.12381001E+01-4.22198783E+04    4
cyC6H12                C   6H  12O   0    0G   200.000  6000.00  1000.0      1
 1.32145970E+01 3.58243434E-02-1.32110852E-05 2.17202521E-09-1.31730622E-13    2
-2.28092102E+04-5.53518322E+01 4.04357527E+00-6.19608335E-03 1.76622274E-04    3
-2.22968474E-07 8.63668578E-11-1.69203544E+04 8.52527441E+00-1.48294969E+04    4
cyC6H11                C   6H  11O   0    0G   200.000  6000.00  1000.0      1
 0.57261502E+01 0.49173558E-01-0.23796767E-04 0.54208507E-08-0.47445368E-12    2
 0.10056946E+04-0.11973133E+02-0.10741222E+01 0.34294293E-01 0.64592225E-04    3
-0.10261825E-06 0.40853054E-10 0.45268762E+04 0.31367410E+02 0.61161896E+04    4
cyC6H10                C   6H  10O   0    0G   200.000  6000.00  1000.0      1
 0.39442769E+01 0.47473657E-01-0.23199637E-04 0.53766657E-08-0.47931014E-12    2
-0.44509693E+04-0.29390438E+00-0.27517028E+01 0.48912768E-01 0.19511676E-04    3
-0.59644226E-07 0.27082294E-10-0.19687471E+04 0.37948748E+02-0.54967525E+03    4
cyC6H9             A05/05C   6H   9O   0    0G   200.000  6000.00  1000.0      1
 0.48230902E+01 0.43906891E-01-0.21524326E-04 0.49885999E-08-0.44431982E-12    2
 0.10570260E+05-0.50750458E+01-0.43595073E+01 0.60597409E-01-0.13999007E-04    3
-0.24483785E-07 0.13990165E-10 0.13380358E+05 0.44118420E+02 0.14606688E+05    4
cyC5H8             g 1/93C   5H   8O   0    0G   200.000  6000.00  1000        1
 9.64282423E+00 2.42562834E-02-8.72089503E-06 1.41190868E-09-8.47267848E-14    2
-1.29253168E+03-3.01225606E+01 2.68980514E+00 2.09635533E-03 1.13034459E-04    3
-1.54077581E-07 6.27623564E-11 2.45828931E+03 1.53075040E+01 4.07720960E+03    4
cyC5H7             A 9/04C   5H   7O   0    0G   200.000  6000.00   1000       1
 9.74013709E+00 2.15079576E-02-7.71169114E-06 1.24352828E-09-7.43887470E-14    2
 1.56355223E+04-2.89664925E+01 2.31203194E+00 7.01023600E-03 9.35725543E-05    3
-1.33744658E-07 5.55553794E-11 1.91721662E+04 1.72892593E+01 2.07617132E+04    4
cyC6H8             T 1/90C   6H   8O   0    0G   200.000  6000.00   1000       1
 0.57911078E+01 0.38887445E-01-0.19353118E-04 0.45417154E-08-0.40833894E-12    2
 0.85461589E+04-0.95072842E+01 0.17881209E+01 0.14442450E-01 0.95904952E-04    3
-0.14190881E-06 0.59226641E-10 0.11037921E+05 0.18868425E+02 0.12806110E+05    4
!C6H7C  cyclohexadienyl radical 1,4 cyCLO
cyC6H7             T 6/93C   6H   7O   0    0G   200.000  6000.00   1000.0     1
 0.12801758E+02 0.21924749E-01-0.79713001E-05 0.12972935E-08-0.78100416E-13    2
 0.17889539E+05-0.45804341E+02-0.10303140E+00 0.34393354E-01 0.39788466E-04    3
-0.85116612E-07 0.39012224E-10 0.22425515E+05 0.26022350E+02 0.24125213E+05    4
C3H4O CH2=CH-CHO  A10/04C   3H   4O   1    0G   200.000  6000.00   1000.0     1
 7.31820729E+00 1.27398510E-02-4.60112009E-06 7.44735077E-10-4.46993049E-14    2
-1.16137229E+04-1.11884734E+01 3.98487241E+00 3.40751550E-03 4.81227535E-05    3
-6.61399005E-08 2.67817331E-11-9.83297241E+03 1.03960574E+01-8.18632872E+03    4
cyC6H10OOH             C   6H  11O   2     G   300.00   5000.00   1000.0     1
 0.92613052E+01 0.55409862E-01-0.27657605E-04 0.64468604E-08-0.57481577E-12    2
-0.11509255E+05-0.23691117E+02-0.38172431E+01 0.81355661E-01-0.31709899E-04    3
-0.10022352E-07 0.70721153E-11-0.74649250E+04 0.46310647E+02-0.52862641E+04    4
cyC6H10OH              C   6H  11O   1    0G   300.000  5000.00   1000.0     1
 0.92477067E+01 0.47676280E-01-0.22769330E-04 0.51348806E-08-0.44585760E-12    2
-0.19833803E+05-0.27056919E+02-0.65684827E+01 0.89265062E-01-0.65895351E-04    3
 0.30396457E-07-0.83570395E-11-0.15169822E+05 0.55728945E+02-0.13688958E+05    4
cyC6H10O               C   6H  10O   1    0G   300.000  5000.00   1000.0     1
 0.82693596E+01 0.47693687E-01-0.23209376E-04 0.52852164E-08-0.46154236E-12    2
 0.71558606E+04-0.23023746E+02-0.79129784E+01 0.97729990E-01-0.98452899E-04    3
 0.74110539E-07-0.27907766E-10 0.11684136E+05 0.60265126E+02 0.12929998E+05    4
```

```
cyOOC6H10OOH            C   6H  11O   4     G   300.000  5000.00   1000.0      1
 0.20094503E+01 0.74073855E-01-0.39254193E-04 0.96576588E-08-0.90066937E-12    2
-0.25674718E+05 0.20565845E+02-0.17398958E+01 0.71686526E-01 0.72801188E-05    3
-0.58960561E-07 0.27307535E-10-0.24730231E+05 0.41406273E+02-0.22104883E+05    4
C5H9CHO                 C   6H  10O   1    0G   300.00   5000.00   1000.0      1
 0.75635301E+01 0.43429097E-01-0.20633442E-04 0.47071654E-08-0.41561195E-12    2
-0.19252738E+05-0.72021706E+01 0.10041174E+01 0.64918416E-01-0.48073388E-04    3
 0.21970927E-07-0.51748858E-11-0.17655422E+05 0.25774533E+02-0.14856868E+05    4
cyC6H9O2                C   6H   9O   2     G   300.000  5000.00   1000.0      1
  .17679030E+02  .25136880E-01 -.68573540E-05  .93749450E-09 -.52110810E-13    2
 -.36850520E+05 -.75556950E+02 -.66703370E+01  .78363980E-01 -.43089680E-04    3
  .74025190E-08  .83083400E-12 -.28830110E+05  .55155830E+02                  4
cyC6H11OO   1/6/2015    C   6H  11O   2     G   300.00   5000.00   1000.0      1
-0.20839567E+00 0.68532755E-01-0.35407414E-04 0.85310323E-08-0.78298305E-12    2
-0.13493035E+05 0.24862162E+02 0.76560000E+00 0.29242014E-01 0.99097744E-04    3
-0.14795512E-06 0.59505351E-10-0.12592840E+05 0.27262169E+02-0.10455858E+05    4
cyC6H11OOH          thermC   6H  12O   2    0G   300.000  5000.000  1000.000    1
 0.97023922E+01 0.53913896E-01-0.25763529E-04 0.58358716E-08-0.50979637E-12    2
-0.32524292E+05-0.27509680E+02-0.83765909E+01 0.11498326E+00-0.11832810E-03    3
 0.83489720E-07-0.28593641E-10-0.27921827E+05 0.63724779E+02-0.26205196E+05    4
cyC6H10Ob 23/2/014 thermC   6H  10O   1    0G   300.000  5000.000 1000.000    1
-0.94946020E+01 0.80553090E-01-0.44208480E-04 0.11132126E-07-0.10563421E-11    2
-0.15606945E+05 0.65125482E+02 0.29262009E+01 0.65415817E-02 0.15371109E-03    3
-0.21344824E-06 0.87175623E-10-0.18496486E+05 0.71794684E+01-0.16357950E+05    4
cyC6H10Oc           thermC   6H  10O   1    0G   300.000  5000.000 1000.000    1
-0.95853077E+01 0.80577563E-01-0.44174188E-04 0.11116295E-07-0.10544255E-11    2
-0.25530791E+05 0.61862506E+02 0.16169856E+01 0.11188534E-01 0.14771115E-03    3
-0.21071414E-06 0.87058128E-10-0.28165251E+05 0.98415047E+01-0.26258119E+05    4
cyC6H10Od           thermC   6H  10O   1    0G   300.000  5000.000  1000.000    1
-0.66687497E+00 0.60687596E-01-0.30099302E-04 0.70125266E-08-0.62731530E-12    2
-0.31167893E+05 0.26362479E+02-0.78489570E+01 0.93504999E-01-0.94472350E-04    3
 0.71093411E-07-0.25979669E-10-0.29886581E+05 0.60321458E+02-0.28779168E+05    4
cyC6H10Oa               C   6H  10O   1    0G   300.00   5000.000   1000.0      1
-0.80846809E+01 0.78416058E-01-0.42966125E-04 0.10802297E-07-0.10236452E-11    2
-0.15124674E+05 0.60499401E+02-0.16543292E+01 0.42696025E-01 0.62179263E-04    3
-0.11687253E-06 0.50777343E-10-0.17184963E+05 0.28835473E+02-0.15440221E+05    4
cyOC6H9OOH 4/9/2014     C   6H  10O   3    0G   300.000  5000.000 1381.000    1
 0.31662570E+00 0.69003372E-01-0.36037339E-04 0.87559801E-08-0.80895897E-12    2
-0.42944421E+05 0.28684832E+02-0.83287424E+01 0.12266269E+00-0.15487972E-03    3
 0.12834888E-06-0.46584898E-10-0.42257621E+05 0.65746476E+02-0.40428193E+05    4
cyOC6H9O            thermC   6H   9O   2    0G   300.000  5000.000  1000.00     1
 0.50515201E+01 0.52248445E-01-0.24442443E-04 0.54446730E-08-0.47112108E-12    2
-0.26071420E+05-0.10519635E+01-0.12527160E+02 0.14264387E+00-0.22347946E-03    3
 0.21324178E-06-0.82059264E-10-0.22976428E+05 0.80631675E+02-0.21965360E+05    4
C6H10O   4/9/14         C   6H  10O   1    0G   300.00  3000.000  1000.0      1
 0.75635301E+01 0.43429097E-01-0.20633442E-04 0.47071654E-08-0.41561195E-12    2
-0.19252738E+05-0.72021706E+01 0.10041174E+01 0.64918416E-01-0.48073388E-04    3
 0.21970927E-07-0.51748858E-11-0.17655422E+05 0.25774533E+02-0.14856868E+05    4
cyC6H11O                C   6H  11O   1    0G   300.000  5000.00   1000.0      1
 0.32637255E+01 0.58784029E-01-0.29394748E-04 0.68775840E-08-0.61578610E-12    2
-0.12963675E+05 0.23642621E+01-0.38078981E+01 0.57665454E-01 0.17189370E-04    3
-0.53677606E-07 0.21536939E-10-0.10152550E+05 0.43686705E+02-0.86709165E+04    4
cyC6H9OH                C   6H  10O   1    0G   300.000  5000.000 1391.000   21
 1.99067050e+01 2.32067426e-02-7.88571110e-06 1.22042324e-09-7.06979066e-14    2
-3.05212139e+04-8.49671185e+01-7.13879294e+00 8.94711849e-02-7.01529641e-05    3
 2.78720200e-08-4.44569042e-12-2.15331030e+04 5.90327460e+01                  4
```

```
cyC6H9OO                C   6H   9O   2    0G   300.000  5000.000 1000.000     1
-0.15752926E+01 0.63566897E-01-0.33475432E-04 0.82122290E-08-0.76530877E-12    2
 0.22864969E+04 0.36636285E+02-0.16012226E+01 0.51507380E-01 0.25977280E-04    3
-0.73889337E-07 0.33956656E-10 0.21056130E+04 0.37835261E+02 0.40149146E+04    4
cyC6H8OOH               C   6H   9O   2     G   300.00   5000.00   1000.0     1
 0.65407841E+01 0.49378665E-01-0.25554660E-04 0.62086740E-08-0.57419865E-12    2
 0.87506338E+04-0.54098324E+01 0.47690303E+00 0.60864654E-01-0.18222490E-04    3
-0.15492520E-07 0.83620658E-11 0.10265509E+05 0.26325566E+02 0.12922781E+05    4
cyOOHC6H9OOH            C   6H  11O   4     G   300.000  5000.00   1376.0     1
 0.13296721E+02 0.56179584E-01-0.28298589E-04 0.66759657E-08-0.60158400E-12    2
-0.21992272E+05-0.40186252E+02-0.55936490E+01 0.12238953E+00-0.13187643E-03    3
 0.97940639E-07-0.35615990E-10-0.17494214E+05 0.54214822E+02-0.14713736E+05    4
cyC9H18                 C   9H  18O   0     G   300.00   5000.00   1000.0     1
 0.91952098E+01 0.76359983E-01-0.36649377E-04 0.83488183E-08-0.73285359E-12    2
-0.31204353E+05-0.27501655E+02-0.14794359E+00 0.53493833E-01 0.98269309E-04    3
-0.16108786E-06 0.65989318E-10-0.26386286E+05 0.32243718E+02-0.23474862E+05    4
cyC9H17A                C   9H  17O   0     G   300.00   5000.00   1000.0     1
 0.10420926E+02 0.71711337E-01-0.34433853E-04 0.78457810E-08-0.68870347E-12    2
-0.83488932E+04-0.31698080E+02-0.79985889E+00 0.60214048E-01 0.75997868E-04    3
-0.13892520E-06 0.58364008E-10-0.33078349E+04 0.36254267E+02-0.44864085E+03    4
cyC9H17B                C   9H  17O   0     G   300.00   5000.00   1000.0     1
 0.95442228E+01 0.72966720E-01-0.35412126E-04 0.81482497E-08-0.72114485E-12    2
-0.97711297E+04-0.27506533E+02-0.11952671E+01 0.64272244E-01 0.60395188E-04    3
-0.11684613E-06 0.47893961E-10-0.50946000E+04 0.36981070E+02-0.22720712E+04    4
cyC9H17E                C   9H  17O   0     G   300.00   5000.00   1000.0     1
 0.10164060E+02 0.71903010E-01-0.34451684E-04 0.78335008E-08-0.68635020E-12    2
-0.10081320E+05-0.31074005E+02-0.11013488E+01 0.63369022E-01 0.63629275E-04    3
-0.12174952E-06 0.50610720E-10-0.51062294E+04 0.36608263E+02-0.22756796E+04    4
cyC9H17OA               C   9H  17O   1     G   300.00   5000.00   1000.0     1
 0.70483926E+01 0.81874052E-01-0.39992306E-04 0.92279487E-08-0.81846201E-12    2
-0.22104321E+05-0.11560038E+02-0.23693395E+01 0.78001500E-01 0.29813060E-04    3
-0.80810957E-07 0.32690154E-10-0.18210765E+05 0.44101034E+02-0.15334376E+05    4
cyC9H17OB               C   9H  17O   1     G   300.00   5000.00   1000.0     1
-0.27191367E+00 0.96568710E-01-0.49448799E-04 0.11853856E-07-0.10845570E-11    2
-0.21136976E+05 0.27189160E+02-0.13690808E+01 0.69999292E-01 0.57246557E-04    3
-0.11586237E-06 0.47581492E-10-0.20124373E+05 0.38395423E+02-0.17125331E+05    4
cyC9H17OE               C   9H  17O   1     G   300.00   5000.00   1000.0     1
-0.27191367E+00 0.96568710E-01-0.49448799E-04 0.11853856E-07-0.10845570E-11    2
-0.21136976E+05 0.27189160E+02-0.13690808E+01 0.69999292E-01 0.57246557E-04    3
-0.11586237E-06 0.47581492E-10-0.20124373E+05 0.38395423E+02-0.17125331E+05    4
cyC9H17OOA              C   9H  17O   2     G   300.00   5000.00   1000.0     1
 0.17905567E+01 0.95046854E-01-0.48137915E-04 0.11462624E-07-0.10439043E-11    2
-0.21588758E+05 0.20264210E+02 0.14434546E+01 0.53201007E-01 0.10570631E-03    3
-0.17111592E-06 0.69868067E-10-0.20137899E+05 0.30717162E+02-0.16717585E+05    4
cyC9H17OOB              C   9H  17O   2     G   300.00   5000.00   1000.0     1
 0.40072499E+01 0.91733442E-01-0.46410142E-04 0.11043285E-07-0.10049520E-11    2
-0.24577890E+05 0.69504200E+01 0.10393619E+01 0.55801806E-01 0.10551449E-03    3
-0.17621272E-06 0.73213815E-10-0.22315479E+05 0.31285161E+02-0.18910272E+05    4
cyC9H17OOE              C   9H  17O   2     G   300.00   5000.00   1000.0     1
 0.40072499E+01 0.91733442E-01-0.46410142E-04 0.11043285E-07-0.10049520E-11    2
-0.24577890E+05 0.69504200E+01 0.10393619E+01 0.55801806E-01 0.10551449E-03    3
-0.17621272E-06 0.73213815E-10-0.22315479E+05 0.31285161E+02-0.18910272E+05    4
cyC9H16OOHA             C   9H  17O   2     G   300.00   5000.00   1000.0     1
 0.10748957E+02 0.79414083E-01-0.38987535E-04 0.90656664E-08-0.80982558E-12    2
-0.19460747E+05-0.25862208E+02-0.30253046E+01 0.10185109E+00-0.24344649E-04    3
-0.31729461E-07 0.16671323E-10-0.15083401E+05 0.48756656E+02-0.11732018E+05    4
```

```
cyC9H16OOHB             C   9H  17O   2     G   300.00   5000.00   1000.0      1
 0.13379544E+02 0.75558327E-01-0.37273422E-04 0.87134659E-08-0.78166287E-12    2
-0.18194927E+05-0.40717780E+02-0.14823267E+01 0.96789973E-01-0.10639837E-04    3
-0.48079169E-07 0.22998514E-10-0.13384618E+05 0.40381780E+02-0.97065191E+04    4
cyC9H16OOHC             C   9H  17O   2     G   300.00   5000.00   1000.0      1
 0.13079428E+02 0.75845037E-01-0.37068002E-04 0.85903464E-08-0.76512728E-12    2
-0.22486759E+05-0.39784732E+02-0.34865105E+01 0.10488697E+00-0.25693708E-04    3
-0.35545644E-07 0.19515581E-10-0.17255360E+05 0.49561458E+02-0.13924705E+05    4
cyC9H16OOHD             C   9H  17O   2     G   300.00   5000.00   1000.0      1
 0.15401219E+02 0.70363174E-01-0.32980931E-04 0.73503939E-08-0.63254893E-12    2
-0.21229854E+05-0.51583547E+02-0.29225305E+01 0.99069395E-01-0.17481873E-04    3
-0.40492000E-07 0.21326349E-10-0.14856749E+05 0.48994422E+02-0.11552803E+05    4
cyC9H16OOHE             C   9H  17O   2     G   300.00   5000.00   1000.0      1
 0.13184783E+02 0.75595731E-01-0.37180434E-04 0.86696545E-08-0.77613429E-12    2
-0.20019736E+05-0.40432633E+02-0.14328604E+01 0.97052827E-01-0.14634502E-04    3
-0.41122371E-07 0.19621659E-10-0.15277505E+05 0.39310299E+02-0.11596103E+05    4
cyC9H16OB               C   9H  16O   1     G   300.00   5000.00   1000.0      1
-0.66633388E+01 0.10590091E+00-0.55888225E-04 0.13705134E-07-0.12761440E-11    2
-0.23510629E+05 0.61354978E+02-0.17429795E+01 0.59311669E-01 0.94891932E-04    3
-0.16743840E-06 0.70734436E-10-0.24512656E+05 0.40944030E+02-0.21858311E+05    4
cyC9H16OE               C   9H  16O   1     G   300.00   5000.00   1000.0      1
-0.58157038E+02 0.24660664E+00-0.17117590E-03 0.50426786E-07-0.53262022E-11    2
-0.12876039E+05 0.32996939E+03-0.11214706E+01 0.77783679E-01 0.69980822E-04    3
-0.15269108E-06 0.68085115E-10-0.29788496E+05 0.33579374E+02-0.26320664E+05    4
cyOOC9H16OOHA           C   9H  17O   4     G   300.00   5000.00   1000.0      1
 0.39083065E+01 0.10080667E+00-0.52144588E-04 0.12635163E-07-0.11662546E-11    2
-0.33737192E+05 0.15813003E+02-0.95037780E+00 0.94784284E-01 0.16210539E-04    3
-0.84721032E-07 0.38698014E-10-0.32286164E+05 0.43706421E+02-0.28366611E+05    4
cyOOC9H16OOHB           C   9H  17O   4     G   300.00   5000.00   1000.0      1
 0.39083065E+01 0.10080667E+00-0.52144588E-04 0.12635163E-07-0.11662546E-11    2
-0.33737192E+05 0.15813003E+02-0.95037780E+00 0.94784284E-01 0.16210539E-04    3
-0.84721032E-07 0.38698014E-10-0.32286164E+05 0.43706421E+02-0.28366611E+05    4
cyOOC9H16OOHD           C   9H  17O   4     G   300.00   5000.00   1000.0      1
 0.39083065E+01 0.10080667E+00-0.52144588E-04 0.12635163E-07-0.11662546E-11    2
-0.33737192E+05 0.15813003E+02-0.95037780E+00 0.94784284E-01 0.16210539E-04    3
-0.84721032E-07 0.38698014E-10-0.32286164E+05 0.43706421E+02-0.28366611E+05    4
cyOOC9H16OOHC           C   9H  17O   4     G   300.00   5000.00   1000.0      1
-0.42720975E+02 0.22784206E+00-0.15467959E-03 0.45047734E-07-0.47258926E-11    2
-0.24855344E+05 0.26176394E+03-0.11372518E+01 0.10624691E+00 0.16473142E-04    3
-0.96308634E-07 0.45211011E-10-0.37340687E+05 0.45167114E+02-0.32985326E+05    4
cyOOC9H16OOHE           C   9H  17O   4     G   300.00   5000.00   1000.0      1
-0.42720975E+02 0.22784206E+00-0.15467959E-03 0.45047734E-07-0.47258926E-11    2
-0.24855344E+05 0.26176394E+03-0.11372518E+01 0.10624691E+00 0.16473142E-04    3
-0.96308634E-07 0.45211011E-10-0.37340687E+05 0.45167114E+02-0.32985326E+05    4
cyOC9H15OOHA            C   9H  16O   3     G   300.00   5000.00   1000.0      1
 0.11710797E+02 0.79255336E-01-0.39301516E-04 0.92120885E-08-0.82814505E-12    2
-0.53014340E+05-0.30299981E+02-0.34201154E+01 0.11390334E+00-0.54430855E-04    3
-0.26766992E-08 0.66650870E-11-0.48690764E+05 0.49226952E+02-0.45134713E+05    4
cyOC9H15OOHB            C   9H  16O   3     G   300.00   5000.00   1000.0      1
 0.13303712E+02 0.77450515E-01-0.38336059E-04 0.89654837E-08-0.80419687E-12    2
-0.53615539E+05-0.38936841E+02-0.70727071E+01 0.13878641E+00-0.10816016E-03    3
 0.48366069E-07-0.11349414E-10-0.48373471E+05 0.64897407E+02-0.45182824E+05    4
cyOC9H15OOHC            C   9H  16O   3     G   300.00   5000.00   1000.0      1
 0.78105236E+01 0.86293176E-01-0.43480130E-04 0.10313797E-07-0.93606097E-12    2
-0.55231047E+05-0.84471664E+01-0.43148147E+01 0.11757905E+00-0.64402111E-04    3
 0.95905222E-08 0.15379953E-11-0.52088647E+05 0.54109394E+02-0.48702189E+05    4
```

```
cyOC9H15OOHD            C   9H  16O   3     G   300.00   5000.00   1000.0      1
 0.11710797E+02 0.79255336E-01-0.39301516E-04 0.92120885E-08-0.82814505E-12    2
-0.53014340E+05-0.30299981E+02-0.34201154E+01 0.11390334E+00-0.54430855E-04    3
-0.26766992E-08 0.66650870E-11-0.48690764E+05 0.49226952E+02-0.45134713E+05    4
cyOC9H15OOHE            C   9H  16O   3     G   300.00   5000.00   1000.0      1
-0.94059667E+01 0.12697325E+00-0.76327461E-04 0.20687994E-07-0.20724292E-11    2
-0.49545963E+05 0.83500517E+02-0.11084056E+02 0.17835645E+00-0.23085326E-03    3
 0.19196706E-06-0.68608665E-10-0.51563394E+05 0.80513083E+02-0.48637238E+05    4
cyC9H16B                C   9H  16O   0     G   300.00   5000.00   1000.0      1
 0.96735214E+01 0.69694074E-01-0.33458856E-04 0.76116127E-08-0.66690399E-12    2
-0.16086511E+05-0.29254598E+02-0.15364952E+01 0.58624106E-01 0.73882555E-04    3
-0.13393382E-06 0.55812576E-10-0.11031518E+05 0.38642658E+02-0.84724561E+04    4
cyC9H16E                C   9H  16O   0     G   300.00   5000.00   1000.0      1
-0.98741851E+01 0.11426439E+00-0.69756383E-04 0.19213268E-07-0.19505417E-11    2
-0.98316749E+04 0.77110458E+02-0.26063579E+01 0.76251152E-01 0.24305665E-04    3
-0.86226171E-07 0.40087880E-10-0.11494726E+05 0.42525170E+02-0.88224681E+04    4
cyC8H15                 C   8H  15O   0     G   300.00   5000.00   1000.0      1
 0.69468033E+01 0.69421069E-01-0.33695825E-04 0.77029722E-08-0.67709104E-12    2
-0.77353218E+04-0.40988039E+01 0.16464935E+00 0.47282117E-01 0.80272684E-04    3
-0.13071350E-06 0.52687046E-10-0.39419027E+04 0.40703145E+02-0.13182584E+04    4
cyC8H14                 C   8H  14O   0     G   300.00   5000.00   1000.0      1
 0.78654704E+01 0.62866484E-01-0.30442163E-04 0.69650905E-08-0.61282577E-12    2
-0.12457594E+05-0.21337426E+02-0.19747157E+01 0.51246588E-01 0.69925785E-04    3
-0.12368386E-06 0.51125158E-10-0.79488034E+04 0.38687246E+02-0.58648064E+04    4
cyC7H13                 C   7H  13O   0     G   300.00   5000.00   1000.0      1
 0.71408111E+01 0.57308382E-01-0.27817891E-04 0.63739674E-08-0.56139155E-12    2
-0.15188928E+04-0.18381169E+02-0.17230503E+01 0.46438908E-01 0.63884325E-04    3
-0.11257107E-06 0.46411221E-10 0.25540375E+04 0.35771775E+02 0.44659610E+04    4
cyC7H12                 C   7H  12O   0     G   300.00   5000.00   1000.0      1
 0.65910481E+01 0.54669101E-01-0.26431343E-04 0.60188932E-08-0.52671280E-12    2
-0.99129199E+04-0.16499202E+02 0.26798144E-01 0.36170673E-01 0.71084959E-04    3
-0.11058525E-06 0.43621053E-10-0.62834065E+04 0.26416415E+02-0.42398364E+04    4
CH2CHOO                0C   2H   3O   2     G   300.00   5000.00  1000.00      1
-0.14222164E+02 0.54411336E-01-0.35422672E-04 0.10029277E-07-0.10315567E-11    2
 0.17393746E+05 0.10563702E+03 0.60130317E+01-0.64387400E-02 0.49703016E-04    3
-0.55498552E-07 0.19940366E-10 0.11395932E+05 0.74410390E+00 0.13240318E+05    4
C3H2OOH                 H   3C   3O   2     G   100.000  5000.000 1273.84      1
 1.16077920E+01 9.66257894E-03-3.98710184E-06 7.42677739E-10-5.17862503E-14    2
 3.39066142E+04-3.12846773E+01 3.92818896E+00 2.74300432E-02-1.74348201E-05    3
 3.86894959E-09 1.02338006E-13 3.63781170E+04 9.64509185E+00                   4
H2CCHCO                0C   3H   3O   1     G   200.000  6000.000 1000.00      1
 6.90703955E+00 1.02341927E-02-3.65649593E-06 5.87914100E-10-3.51359226E-14    2
 7.62708561E+03-7.29856114E+00 4.11237192E+00 5.05829116E-03 3.17832265E-05    3
-4.55489258E-08 1.86325507E-11 8.99713585E+03 1.01743843E+01 1.06476509E+04    4
C3H3OO                  H   3C   3O   2     G   100.000  5000.000 1277.13      1
 8.15144842E+00 1.32714890E-02-5.21066762E-06 8.40167102E-10-5.04794326E-14    2
 2.90557766E+04-1.13406281E+01 2.05657379E+00 3.73710595E-02-3.94004261E-05    3
C2H3CO                  H   3O   1C   3    0G   300.000  5000.000 1402.000    01
 9.37467676E+00 7.91296900E-03-2.67198280E-06 4.11115430E-10-2.36978981E-14    2
 1.92969514E+03-2.40892696E+01 1.36242013E+00 3.15273972E-02-3.00218935E-05    3
 1.48167112E-08-2.87971530E-12 4.25770215E+03 1.72626546E+01                   4
sC3H5OOH                C   3H   6O   2     G   300.00   5000.00   1000.0      1
 0.91497940E+01 0.20233793E-01-0.91925428E-05 0.20209201E-08-0.17236897E-12    2
-0.11404608E+05-0.18272595E+02 0.31193916E+01 0.41796642E-01-0.49802136E-04    3
 0.44016030E-07-0.17090638E-10-0.97342228E+04 0.12357094E+02-0.73093577E+04    4
pC3H5OOH                C   3H   6O   2     G   300.00   5000.00   1000.0      1
 0.37312177E+01 0.30497990E-01-0.15358390E-04 0.36770888E-08-0.33749669E-12    2
-0.85567392E+04 0.11850166E+02-0.16477257E+01 0.64109955E-01-0.86825387E-04    3
 0.70910820E-07-0.24343837E-10-0.81686108E+04 0.34718465E+02-0.64505653E+04    4
```

```
C3H5O      4/24/92 THERMC   3H   5O   1    0G   300.000  5000.000 1375.000    21
 9.93380796E+00 1.21383493E-02-4.23299952E-06 6.65805507E-10-3.89817563E-14    2
 6.20904655E+03-2.68841926E+01 1.48979417E+00 2.77306345E-02-1.35044719E-05    3
 2.24225811E-09 8.28232368E-14 9.58557792E+03 1.99841620E+01                   4
C2H5CHO                 C   3H   6O   1    0G   300.000  5000.000 1000.000     1
-0.33290446E+01 0.41180459E-01-0.23805156E-04 0.62698432E-08-0.61475717E-12    2
-0.22484570E+05 0.44822898E+02 0.14741130E+01 0.35244562E-01-0.30509905E-04    3
 0.20361759E-07-0.68880848E-11-0.24353176E+05 0.17803159E+02-0.22581188E+05    4
END
```

Appendix III

Transport properties (trandat)

AR	0	136.500	3.330	0.000	0.000	0.000
C	0	71.400	3.298	0.000	0.000	0.000
C2	1	97.530	3.621	0.000	1.760	4.000
C2O	1	232.400	3.828	0.000	0.000	1.000
CN2	1	232.400	3.828	0.000	0.000	1.000
C2H	1	209.000	4.100	0.000	0.000	2.500
C2H2	1	209.000	4.100	0.000	0.000	2.500
C2H2OH	2	224.700	4.162	0.000	0.000	1.000
C2H3	2	209.000	4.100	0.000	0.000	1.000
C2H4	2	280.800	3.971	0.000	0.000	1.500
C2H5	2	252.300	4.302	0.000	0.000	1.500
C2H6	2	252.300	4.302	0.000	0.000	1.500
C2N	1	232.400	3.828	0.000	0.000	1.000
C2N2	1	349.000	4.361	0.000	0.000	1.000
C3H2	2	209.000	4.100	0.000	0.000	1.000
C3H4	1	252.000	4.760	0.000	0.000	1.000
C3H6	2	266.800	4.982	0.000	0.000	1.000
C3H7	2	266.800	4.982	0.000	0.000	1.000
C4H6	2	357.000	5.180	0.000	0.000	1.000
I*C3H7	2	266.800	4.982	0.000	0.000	1.000
!N*C3H7	2	266.800	4.982	0.000	0.000	1.000
!nC3H7	2	266.800	4.982	0.000	0.000	1.000
C3H8	2	266.800	4.982	0.000	0.000	1.000
C4H	1	357.000	5.180	0.000	0.000	1.000
C4H2	1	357.000	5.180	0.000	0.000	1.000
C4H2OH	2	224.700	4.162	0.000	0.000	1.000
C4H8	2	357.000	5.176	0.000	0.000	1.000
C4H9	2	357.000	5.176	0.000	0.000	1.000
I*C4H9	2	357.000	5.176	0.000	0.000	1.000
C5H2	1	357.000	5.180	0.000	0.000	1.000
C5H3	1	357.000	5.180	0.000	0.000	1.000
C6H2	1	357.000	5.180	0.000	0.000	1.000
C6H5	2	412.300	5.349	0.000	0.000	1.000
C6H5O	2	450.000	5.500	0.000	0.000	1.000
C5H5OH	2	450.000	5.500	0.000	0.000	1.000
C6H6	2	412.300	5.349	0.000	0.000	1.000
C6H7	2	412.300	5.349	0.000	0.000	1.000
CH	1	80.000	2.750	0.000	0.000	0.000
CH2	1	144.000	3.800	0.000	0.000	0.000
CH2(S)	1	144.000	3.800	0.000	0.000	0.000
CH2*	1	144.000	3.800	0.000	0.000	0.000
CH2CHCCH	2	357.000	5.180	0.000	0.000	1.000
CH2CHCCH2	2	357.000	5.180	0.000	0.000	1.000
CH2CHCH2	2	260.000	4.850	0.000	0.000	1.000
CH2CHCHCH	2	357.000	5.180	0.000	0.000	1.000
CH2CHCHCH2	2	357.000	5.180	0.000	0.000	1.000
CH2CO	2	436.000	3.970	0.000	0.000	2.000
CH2O	2	498.000	3.590	0.000	0.000	2.000
CH2OH	2	417.000	3.690	1.700	0.000	2.000
CH3	1	144.000	3.800	0.000	0.000	0.000
CH3CC	2	252.000	4.760	0.000	0.000	1.000
CH3CCCH2	2	357.000	5.180	0.000	0.000	1.000
CH3CCCH3	2	357.000	5.180	0.000	0.000	1.000

CH3CCH2	2	260.000	4.850	0.000	0.000	1.000
CH3CHCH	2	260.000	4.850	0.000	0.000	1.000
CH3CH2CCH	2	357.000	5.180	0.000	0.000	1.000
CH3CHO	2	436.000	3.970	0.000	0.000	2.000
CH2CHO	2	436.000	3.970	0.000	0.000	2.000
CH3CO	2	436.000	3.970	0.000	0.000	2.000
CH3O	2	417.000	3.690	1.700	0.000	2.000
CH3OH	2	481.800	3.626	0.000	0.000	1.000
CH4	2	141.400	3.746	0.000	2.600	13.00
CH4O	2	417.000	3.690	1.700	0.000	2.000
CN	1	75.000	3.856	0.000	0.000	1.000
CNC	1	232.400	3.828	0.000	0.000	1.000
CNN	1	232.400	3.828	0.000	0.000	1.000
CO	1	98.100	3.650	0.000	1.950	1.800
CO2	1	244.000	3.763	0.000	2.650	2.100
H	0	145.000	2.050	0.000	0.000	0.000
H2C4O	2	357.000	5.180	0.000	0.000	1.000
H2	1	38.000	2.920	0.000	0.790	280.0
H2CCCCH	2	357.000	5.180	0.000	0.000	1.000
H2CCCCH2	2	357.000	5.180	0.000	0.000	1.000
H2CCCH	2	252.000	4.760	0.000	0.000	1.000
H2CN	1	569.000	3.630	0.000	0.000	1.000
H2NO	2	116.700	3.492	0.000	0.000	1.000
H2O	2	572.400	2.605	1.844	0.000	4.000
H2O2	2	107.400	3.458	0.000	0.000	3.800
HC2N2	1	349.000	4.361	0.000	0.000	1.000
HCCHCCH	2	357.000	5.180	0.000	0.000	1.000
HCCO	2	150.000	2.500	0.000	0.000	1.000
HCNN	2	150.000	2.500	0.000	0.000	1.000
HCCOH	2	436.000	3.970	0.000	0.000	2.000
HCN	1	569.000	3.630	0.000	0.000	1.000
HCO	2	498.000	3.590	0.000	0.000	0.000
HE	0	10.200	2.576	0.000	0.000	0.000
HCNO	2	232.400	3.828	0.000	0.000	1.000
HOCN	2	232.400	3.828	0.000	0.000	1.000
HNCO	2	232.400	3.828	0.000	0.000	1.000
HNNO	2	232.400	3.828	0.000	0.000	1.000
HNO	2	116.700	3.492	0.000	0.000	1.000
HNOH	2	116.700	3.492	0.000	0.000	1.000
HO2	2	107.400	3.458	0.000	0.000	1.000
N	0	71.400	3.298	0.000	0.000	0.000
N2	1	97.530	3.621	0.000	1.760	4.000
N2H2	2	71.400	3.798	0.000	0.000	1.000
N2H3	2	200.000	3.900	0.000	0.000	1.000
N2H4	2	205.000	4.230	0.000	4.260	1.500
N2O	1	232.400	3.828	0.000	0.000	1.000
NCN	1	232.400	3.828	0.000	0.000	1.000
NCO	1	232.400	3.828	0.000	0.000	1.000
NH	1	80.000	2.650	0.000	0.000	4.000
NH2	2	80.000	2.650	0.000	2.260	4.000
NH3	2	481.000	2.920	1.470	0.000	10.00
NNH	2	71.400	3.798	0.000	0.000	1.000
NO	1	97.530	3.621	0.000	1.760	4.000
NCNO	2	232.400	3.828	0.000	0.000	1.000
NO2	2	200.000	3.500	0.000	0.000	1.000
O	0	80.000	2.750	0.000	0.000	0.000
O2	1	107.400	3.458	0.000	1.600	3.800
OH	1	80.000	2.750	0.000	0.000	0.000
c-C6H4	2	464.800	5.29	0.00	10.32	1.000

A1	2	464.800	5.29	0.00	10.32	1.000
A1-	2	464.800	5.29	0.00	10.32	1.000
c-C6H7	2	464.800	5.29	0.00	10.32	1.000
A1CH3	2	495.300	5.68	0.43	12.30	1.000
A1C2H	2	535.600	5.72	0.77	12.00	1.000
A1C2H*	2	535.600	5.72	0.77	12.00	1.000
A1C2H-	2	535.600	5.72	0.77	12.00	1.000
A1C2H3	2	546.200	6.00	0.13	15.00	1.000
A1C2H3*	2	546.200	6.00	0.13	15.00	1.000
n-A1C2H2	2	546.200	6.00	0.13	15.00	1.000
i-A1C2H2	2	546.200	6.00	0.13	15.00	1.000
naphthyne	2	630.400	6.18	0.00	16.50	1.000
A2	2	630.400	6.18	0.00	16.50	1.000
A2-	2	630.400	6.18	0.00	16.50	1.000
A2-1	2	630.400	6.18	0.00	16.50	1.000
A2-2	2	630.400	6.18	0.00	16.50	1.000
A1C2HC2H2	2	630.400	6.18	0.00	16.50	1.000
A1C2H)2	2	630.400	6.18	0.00	16.50	1.000
A2R5	2	693.100	6.47	0.00	18.00	1.000
A2R5-	2	693.100	6.47	0.00	18.00	1.000
A2R5C2H*	2	772.800	6.937	0.000	0.000	0.000
A2R5C2H	2	772.800	6.937	0.000	0.000	0.000
A2C2H	2	693.100	6.47	0.00	18.00	1.000
A2C2H2	2	693.100	6.47	0.00	18.00	1.000
A2C2H*	2	693.100	6.47	0.00	18.00	1.000
A2C2HA	2	693.100	6.47	0.00	18.00	1.000
A2C2HA*	2	693.100	6.47	0.00	18.00	1.000
A2C2HB	2	693.100	6.47	0.00	18.00	1.000
A2C2HB*	2	693.100	6.47	0.00	18.00	1.000
A3	2	772.000	6.96	0.00	38.80	1.000
A3R5	2	837.500	7.275	0.000	0.000	0.000
A3-1	2	772.000	6.96	0.00	38.80	1.000
A3-4	2	772.000	6.96	0.00	38.80	1.000
A3R5-	2	837.500	7.275	0.000	0.000	0.000
A2C2H)2	2	772.000	6.96	0.00	38.80	1.000
A3R5AC	2	879.600	7.561	0.000	0.000	0.000
A4	2	834.900	7.24	0.00	45.00	1.000
A4R5	2	879.600	7.561	0.000	0.000	0.000
A4-	2	834.900	7.24	0.00	45.00	1.000
A4R5-	2	879.600	7.561	0.000	0.000	0.000
A3C2H	2	834.900	7.24	0.00	45.00	1.000
A3C2H2	2	834.900	7.24	0.00	45.00	1.000
P2	2	676.500	6.31	0.00	20.00	1.000
P2-H	2	676.500	6.31	0.00	20.00	1.000
P2-	2	676.500	6.31	0.00	20.00	1.000
C5H4O	2	464.800	5.29	0.00	10.32	0.000
C5H5O	2	464.800	5.29	0.00	10.32	0.000
C5H4OH	2	464.800	5.29	0.00	10.32	0.000
C6H5O	2	464.800	5.29	0.00	10.32	0.000
C6H5OH	2	464.800	5.29	0.00	10.32	0.000
INDENYL	2	402.900	6.744	0.00	0.000	1.000
INDENE	2	402.900	6.744	0.00	0.000	1.000
A3C2H	2	879.600	7.561	0.00	0.000	0.000
PYRENE	2	776.200	7.407	0.00	0.000	1.000
A3C2H*	2	879.600	7.561	0.00	0.000	0.000
C18H12	2	879.600	7.561	0.00	0.000	0.000
C18H11	2	879.600	7.561	0.00	0.000	0.000
BAPYR	2	833.062	8.087	0.000	0.000	1.000
BAPYR*S	2	833.062	8.087	0.000	0.000	1.000

BGHIF	2	870.7	7.559	0.000	0.000	1.000
CH3HCO	2	436.000	3.970	0.000	0.000	2.000
A4C2H	2	776.2	7.407	0.000	0.000	1.000
A4C2H*	2	776.2	7.407	0.000	0.000	1.000
NE	0	136.500	3.330	0.000	0.000	0.000
C4H3S	2	367.200	4.933	0.000	0.000	1.000
C8H	1	357.000	5.180	0.000	0.000	1.000
C8H2	1	357.000	5.180	0.000	0.000	1.000
C7H7	2	460.0	5.43	0.0	0.0	0.000
C7H8	2	495.3	5.68	0.43	12.3	0.000
n-C8H7	2	536.200	5.693	0.000	0.000	0.000
A3-	2	837.500	7.275	0.000	0.000	0.000
CH3CO	2	436.000	3.970	0.000	0.000	2.000
CH3CHO	2	436.000	3.970	0.000	0.000	2.000
C3H6O	2	357.000	5.180	0.000	0.000	1.000
C4	2	357.000	5.180	0.000	0.000	1.000
H2CN	1	569.000	3.630	0.000	0.000	1.000
H2NO	2	116.700	3.492	0.000	0.000	1.000
HC2N2	1	349.000	4.361	0.000	0.000	1.000
HCCHCCH	2	357.000	5.180	0.000	0.000	1.000
HCCO	2	150.000	2.500	0.000	0.000	1.000
HCNN	2	150.000	2.500	0.000	0.000	1.000
HCCOH	2	436.000	3.970	0.000	0.000	2.000
C4H	1	357.000	5.180	0.000	0.000	1.000
C4H2	1	357.000	5.180	0.000	0.000	1.000
H2C4O	2	357.000	5.180	0.000	0.000	1.000
C4H2OH	2	224.700	4.162	0.000	0.000	1.000
i-C4H3	2	357.000	5.180	0.000	0.000	1.000
n-C4H3	2	357.000	5.180	0.000	0.000	1.000
H2CCCCH	2	357.000	5.180	0.000	0.000	1.000
C4H4	2	357.000	5.180	0.000	0.000	1.000
i-C4H5	2	357.000	5.180	0.000	0.000	1.000
n-C4H5	2	357.000	5.180	0.000	0.000	1.000
C4H6	2	357.000	5.180	0.000	0.000	1.000
C4H612	2	357.000	5.180	0.000	0.000	1.000
C5H2	1	357.000	5.180	0.000	0.000	1.000
C5H3	1	357.000	5.180	0.000	0.000	1.000
C5H5	1	357.000	5.180	0.000	0.000	1.000
C5H6	1	357.000	5.180	0.000	0.000	1.000
C6H	1	357.000	5.180	0.000	0.000	1.000
C6H2	1	357.000	5.180	0.000	0.000	1.000
C6H3	2	357.000	5.180	0.000	0.000	1.000
l-C6H4	2	412.300	5.349	0.000	0.000	1.000
n-C6H5	2	412.300	5.349	0.000	0.000	1.000
i-C6H5	2	412.300	5.349	0.000	0.000	1.000
l-C6H6	2	412.300	5.349	0.000	0.000	1.000
n-C6H7	2	412.300	5.349	0.000	0.000	1.000
i-C6H7	2	412.300	5.349	0.000	0.000	1.000
C6H8	2	412.300	5.349	0.000	0.000	1.000
C3H5	2	260.000	4.850	0.000	0.000	1.000
CH2HCO	2	436.000	3.970	2.760	0.000	2.000
nC4H7	2	357.000	5.180	0.000	0.000	1.000
C4H8	2	357.000	5.176	0.000	0.000	1.000
C3H8	2	266.800	4.982	0.000	0.000	1.000
CH3CO	2	436.000	3.970	0.000	0.000	2.000
C10H	1	357.000	5.180	0.000	0.000	1.000
C10H2	1	357.000	5.180	0.000	0.000	1.000
C12H	1	357.000	5.180	0.000	0.000	1.000
C12H2	1	357.000	5.180	0.000	0.000	1.000

A2CH3	2	658.602	6.335	0.000	0.000	0.000
A2CH2	2	655.890	6.320	0.000	0.000	0.000
A3CH3	2	879.600	7.561	0.000	0.000	0.000
A3CH2	2	879.600	7.561	0.000	0.000	0.000
A3*	2	772.0	6.96	0.00	38.80	1.000
A3*-	2	772.0	6.96	0.00	38.80	1.000
C2H5O	2	436.000	3.970	0.000	0.000	2.000
C2H5O2	2	436.000	3.970	0.000	0.000	2.000
C2H5O2H	2	436.000	3.970	0.000	0.000	2.000
C2H5OH	2	436.000	3.970	0.000	0.000	2.000
cC3H2	2	209.000	4.100	0.000	0.000	1.000
C3H	2	209.000	4.100	0.000	0.000	1.000
C4H3	2	357.000	5.180	0.000	0.000	1.000
C3H3	2	252.000	4.760	0.000	0.000	1.000
C4H5	2	357.000	5.180	0.000	0.000	1.000
C4H7	2	357.000	5.180	0.000	0.000	1.000
CH3O2	2	481.800	3.626	0.000	0.000	1.000
CH3O2H	2	481.800	3.626	0.000	0.000	1.000
C3H6O	2	403.6	4.968	2.0	0.0	1.0
C2H5O2	2	470.600	4.410	0.000	0.000	1.500
nC4H9O2	2	496.000	5.200	0.000	0.000	1.000
C2H5O2H	2	470.600	4.410	0.000	0.000	1.500
C3H5O2	2	427.0	5.117	2.0	0.0	1.0 !
C3H5O2H	2	427.0	5.117	2.0	0.0	1.0 !
C3H5O	2	411.000	4.820	0.000	0.000	1.000
CH3CO3	2	436.000	3.970	0.000	0.000	2.000
CH3CO3H	2	436.000	3.970	0.000	0.000	2.000
nC3H7O2	2	481.5	4.997	1.7	0.0	1.0
nC3H7O2H	2	481.5	4.997	1.7	0.0	1.0
C2H5O	2	470.600	4.410	0.000	0.000	1.500
sC4H9O	2	496.000	5.200	0.000	0.000	1.000
C2HO	1	232.400	3.828	0.000	0.000	1.000
nC3H7	2	303.400	4.810	0.000	0.000	1.000
nC3H7O	2	481.5	4.997	1.7	0.0	1.0
CH3CHO	2	436.000	3.970	0.000	0.000	2.000
CH3O2CH3	2	357.100	4.720	0.000	0.000	1.000
nC3H7O	2	481.5	4.997	1.7	0.0	1.0
nC3H7O2	2	481.5	4.997	1.7	0.0	1.0
nC3H7O2H	2	481.5	4.997	1.7	0.0	1.0
iC3H7O	2	459.5	5.036	1.7	0.0	1.0
iC3H7O2	2	459.5	5.036	1.7	0.0	1.0
iC3H7O2H	2	459.5	5.036	1.7	0.0	1.0
iC4H10	2	335.7	5.208	0.1	0.0	1.0
nC4H9	2	352.000	5.240	0.000	0.000	1.000
sC4H9	2	352.000	5.240	0.000	0.000	1.000
nC4H9O	2	496.000	5.200	0.000	0.000	1.000
iC4H7	2	355.000	4.650	0.000	0.000	1.000
nC4H9O2	2	496.000	5.200	0.000	0.000	1.000
sC4H9O2	2	496.000	5.200	0.000	0.000	1.000
nC4H9O2H	2	496.000	5.200	0.000	0.000	1.000
sC4H9O2H	2	496.000	5.200	0.000	0.000	1.000
C4H10	2	350.9	5.206	0.0	0.0	1.0
iC3H7	2	303.400	4.810	0.000	0.000	1.000
tC4H9	2	352.000	5.240	0.000	0.000	1.000
iC4H9	2	352.000	5.240	0.000	0.000	1.000
iC4H8	2	344.5	5.089	0.5	0.0	1.0
C4H8O	2	444.197	5.063	0.000	0.000	0.000
C7H16	2	459.6	6.253	0.0	0.0	1.0
iC7H15	2	459.6	6.253	0.0	0.0	1.0

iC7H14	2	459.6	6.253	0.0	0.0	1.0
aC7H14	2	457.8	6.173	0.3	0.0	1.0
cC7H14	2	457.8	6.173	0.3	0.0	1.0
iC7H13	2	457.8	6.173	0.3	0.0	1.0
C7H15O2	2	561.0	6.317	1.7	0.0	1.0
C7H15OO	2	561.0	6.317	1.7	0.0	1.0
C7H15O4	2	600.6	7.229	1.8	0.0	1.0
iC7H14O	2	561.0	6.317	1.7	0.0	1.0
C7H14O3	2	511.5	6.297	0.0	0.0	1.0
aC6H12	2	430.1	5.833	0.0	0.0	1.0
iC6H13	2	422.5	5.870	0.0	0.0	1.0
iC6H12	2	422.5	5.870	0.0	0.0	1.0
C6H11	2	482.473	5.307	0.000	0.000	0.000
iC6H11	2	482.473	5.307	0.000	0.000	0.000
C6H12CHO	2	591.585	5.960	0.000	0.000	0.000
iC7H13O	2	591.585	5.960	0.000	0.000	0.000
C7H13O	2	591.585	5.960	0.000	0.000	0.000
C7H15O	2	591.585	5.960	0.000	0.000	0.000
C6H10	2	426.300	5.510	0.000	0.000	1.000
nC6H14	2	427.4	5.946	0.0	0.0	1.0
C5H10	2	386.2	5.489	0.4	0.0	1.0
iC5H11	2	440.735	5.041	0.000	0.000	0.000
iC5H10	2	440.735	5.041	0.000	0.000	0.000
C5H9O	2	523.2	5.664	1.7	0.0	1.0
iC5H9O	2	523.2	5.664	1.7	0.0	1.0
iC5H10O	2	523.2	5.664	1.7	0.0	1.0
nC5H12	2	391.7	5.591	0.0	0.0	1.0
C5H9	2	396.8	5.458	0.0	0.0	1.0
iC5H9	2	396.8	5.458	0.0	0.0	1.0
C5H8	2	408.000	5.200	0.000	0.000	1.000
iC8H18	2	458.5	6.414	0.0	0.0	1.0
aC8H17	2	458.5	6.414	0.0	0.0	1.0
bC8H17	2	458.5	6.414	0.0	0.0	1.0
cC8H17	2	458.5	6.414	0.0	0.0	1.0
dC8H17	2	458.5	6.414	0.0	0.0	1.0
iC8H17	2	458.5	6.414	0.0	0.0	1.0
iC8H16	2	485.6	6.440	0.3	0.0	1.0
C8H16	2	485.6	6.440	0.3	0.0	1.0
iC8H15	2	485.6	6.440	0.3	0.0	1.0
nC8H15	2	485.6	6.440	0.3	0.0	1.0
aC8H17O2	2	581.3	6.506	2.0	0.0	1.0
bC8H17O2	2	581.3	6.506	2.0	0.0	1.0
cC8H17O2	2	581.3	6.506	2.0	0.0	1.0
dC8H17O2	2	581.3	6.506	2.0	0.0	1.0
aC8H17OO	2	581.3	6.506	2.0	0.0	1.0
bC8H17OO	2	581.3	6.506	2.0	0.0	1.0
cC8H17OO	2	581.3	6.506	2.0	0.0	1.0
aC8H17O4	2	581.3	6.506	2.0	0.0	1.0
bC8H17O4	2	581.3	6.506	2.0	0.0	1.0
cC8H17O4	2	581.3	6.506	2.0	0.0	1.0
C8H16O3	2	581.3	6.506	2.0	0.0	1.0
CH2CH2OH	2	436.000	3.970	0.000	0.000	2.000
CH3CH2O	2	436.000	3.970	0.000	0.000	2.000
CH3CHOH	2	436.000	3.970	0.000	0.000	2.000
N-C12H26	2	789.980	7.047	0.000	0.000	1.000
C12H25	2	789.980	7.047	0.000	0.000	1.000
aC12H25	2	789.980	7.047	0.000	0.000	1.000
bC12H25	2	789.980	7.047	0.000	0.000	1.000
C12H24	2	775.294	7.090	0.000	0.000	1.000

C12H23	2	775.294	7.090	0.000	0.000	1.000
C12H25O2	2	805.031	7.102	0.000	0.000	1.000
C12H24OOH	2	805.031	7.102	0.000	0.000	1.000
O2C12H24OOH	2	877.052	7.457	0.000	0.000	1.000
OOC12H24OOH	2	877.052	7.457	0.000	0.000	1.000
HO2C12H23OOH	2	877.052	7.457	0.000	0.000	1.000
OC12H23OOH	2	877.052	7.457	0.000	0.000	1.000
OC12H23O2H	2	877.052	7.457	0.000	0.000	1.000
OC12H23O	2	805.031	7.102	0.000	0.000	1.000
C11H23	2	750.460	6.834	0.000	0.000	1.000
C11H22	2	763.817	6.688	0.000	0.000	1.000
C10H20	2	698.122	6.578	0.000	0.000	1.000
C9H19	2	660.032	6.467	0.000	0.000	1.000
C9H18	2	655.390	6.331	0.000	0.000	1.000
C8H17	2	613.127	6.250	0.000	0.000	1.000
C6H13	2	422.5	5.870	0.0	0.0	1.0
cyC6H12	2	467.7	5.601	0.61	11.4	2.6
cyC6H11	2	467.7	5.601	0.61	11.2	2.6
cyC6H10	2	468.7	5.521	0.55	10.1	2.7
cyC6H10OOH	2	607.7	5.588	0.55	12.4	1.4
cyC6H9	2	468.7	5.521	0.2	10.9	2.7
cyC5H8	2	440.2	5.235	0.9	9.15	2.9
cyC5H7	2	440.2	5.235	0.2	9.15	2.9
cyC6H8	2	469.5	5.441	0.44	12.3	2.7
cyC6H7	2	469.5	5.441	0.44	13.3	2.7
C3H4O	2	405.7	4.804	2.67	5.66	1.1
cyC6H11OO	2	557.7	5.678	2.9	12.3	1.9
cyOOC6H10OOH	2	557.7	5.678	3.08	13.3	1.8
C5H9CHO	1	493.0	5.845	0.83	10.9	4.4
iC6H11O	2	493.0	5.845	0.83	10.9	4.4
iC6H12O	2	493.0	5.845	0.83	10.9	4.4
C2H3CHO	1	411.6	4.921	2.72	6.29	2.6
C2H3CO	1	411.6	4.921	2.72	6.29	2.5
C4H5O	1	436.8	5.311	2.78	8.20	2.8
C3H3O	1	411.6	4.921	2.72	6.26	2.4
C2H4O	1	442.5	4.725	2.75	6.29	0.5
C2H3O	1	389.6	4.721	2.72	6.29	1.0
C2H2OOH	1	253.9	4.005	1.44	3.33	0.6
C4H6OOH	1	366.8	4.953	0.78	7.41	6.4
cyC6H11O	2	447.95	5.475	0.61	11.8	2.6
cyC6H9OOH	2	607.7	5.588	0.55	10.7	1.4
cyC6H9O	2	469.5	5.4	0.4	11.4	2.7
cyOC6H9OOH	2	607.7	5.6	0.6	12.6	1.4
cyC6H10Oa	2	462.52	5.432	1.74	11.6	2.7
cyC6H10Ob	2	462.52	5.432	1.74	11.6	2.7
cyC6H10Oc	2	462.52	5.432	1.74	11.6	2.7
cyC6H10Od	2	515.20	5.627	2.76	11.6	2.7
N-C16H34	2	661.920	8.494	0.000	0.000	1.000
C16H33	2	667.466	8.631	0.000	0.000	1.000
aC16H33	2	667.466	8.631	0.000	0.000	1.000
bC16H33	2	667.466	8.631	0.000	0.000	1.000
C16H32	2	671.333	8.640	0.000	0.000	1.000
C16H31	2	673.373	8.567	0.000	0.000	1.000
C16H33O2	2	724.821	8.797	0.000	0.000	1.000
C16H32OOH	2	830.913	8.763	0.000	0.000	1.000
OOC16H32OOH	2	889.479	8.934	0.000	0.000	1.000
HOOC16H31OOH	2	994.233	8.921	0.000	0.000	1.000
OC16H31O	2	801.400	8.773	0.000	0.000	1.000
OC16H31OOH	2	904.192	8.879	0.000	0.000	1.000

OC12H23O	2	805.031	7.102	0.000	0.000	1.000
C10H21O2	2	488.49	7.11	1.83	20.01	1.00
C10H20OOH	2	488.08	7.18	1.83	20.18	1.00
O2C10H20OOH	2	518.47	6.92	2.00	21.03	1.00
OC10H20OOH	2	531.95	7.10	2.00	20.35	1.00
N-C10H22	2	523.6	6.87	0.0	0.0	1.0
C10H20	2	482.80	6.28	0.00	0.00	1.00
aC10H21	2	523.6	6.87	0.0	0.0	1.0
bC10H21	2	523.6	6.87	0.0	0.0	1.0
OC12H23OOH	2	877.05	7.457	0.00	0.000	1.00
C5H11	2	440.735	5.041	0.000	0.000	0.000
C7H13	2	457.8	6.173	0.3	0.0	1.0
C7H15	2	459.6	6.253	0.0	0.0	1.0
A2CH2OH	2	658.602	6.335	0.000	0.000	0.000
A2CHO	2	658.602	6.335	0.000	0.000	0.000
A2CO	2	658.602	6.335	0.000	0.000	0.000
A2OH	2	658.602	6.335	0.000	0.000	0.000
A2O	2	658.602	6.335	0.000	0.000	0.000
CH3O2	2	481.800	3.626	0.000	0.000	1.000
CH3O2H	2	481.800	3.626	0.000	0.000	1.000
C3H6O	2	403.6	4.968	2.0	0.0	1.0
C2H3HCO	2	411.000	4.820	0.000	0.000	1.000
CH3CHCO	2	411.000	4.820	0.000	0.000	1.000
C2H5O2	2	470.600	4.410	0.000	0.000	1.500
nC4H9O2	2	496.000	5.200	0.000	0.000	1.000
C2H5O2H	2	470.600	4.410	0.000	0.000	1.500
C3H5O2	2	427.0	5.117	2.0	0.0	1.0
C3H5O2H	2	427.0	5.117	2.0	0.0	1.0
C3H5O	2	411.000	4.820	0.000	0.000	1.000
CH3CO3	2	436.000	3.970	0.000	0.000	2.000
CH3CO3H	2	436.000	3.970	0.000	0.000	2.000
nC3H7O2	2	481.5	4.997	1.7	0.0	1.0
nC3H7O2H	2	481.5	4.997	1.7	0.0	1.0
C2H5O	2	470.600	4.410	0.000	0.000	1.500
sC4H9O	2	496.000	5.200	0.000	0.000	1.000
C2HO	1	232.400	3.828	0.000	0.000	1.000
nC3H7	2	303.400	4.810	0.000	0.000	1.000
nC3H7O	2	481.5	4.997	1.7	0.0	1.0
CH3CHO	2	436.000	3.970	0.000	0.000	2.000
CH3O2CH3	2	357.100	4.720	0.000	0.000	1.000
nC3H7O	2	481.5	4.997	1.7	0.0	1.0
nC3H7O2	2	481.5	4.997	1.7	0.0	1.0
nC3H7O2H	2	481.5	4.997	1.7	0.0	1.0
iC3H7O	2	459.5	5.036	1.7	0.0	1.0
iC3H7O2	2	459.5	5.036	1.7	0.0	1.0
iC3H7O2H	2	459.5	5.036	1.7	0.0	1.0
iC4H10	2	335.7	5.208	0.1	0.0	1.0
nC4H9	2	352.000	5.240	0.000	0.000	1.000
sC4H9	2	352.000	5.240	0.000	0.000	1.000
nC4H9O	2	496.000	5.200	0.000	0.000	1.000
iC4H7	2	355.000	4.650	0.000	0.000	1.000
nC4H9O2	2	496.000	5.200	0.000	0.000	1.000
sC4H9O2	2	496.000	5.200	0.000	0.000	1.000
nC4H9O2H	2	496.000	5.200	0.000	0.000	1.000
sC4H9O2H	2	496.000	5.200	0.000	0.000	1.000
nC4H10	2	350.9	5.206	0.0	0.0	1.0
C4H9OO	2	496.000	5.200	0.000	0.000	1.000
C4H9OOH	2	496.000	5.200	0.000	0.000	1.000
C4H8OOH	2	496.000	5.200	0.000	0.000	1.000

C4H8OOO2H	2	496.000	5.200	0.000	0.000	1.000
C4H7O	2	444.197	5.063	0.000	0.000	0.000
iC4H7O	2	444.197	5.063	0.000	0.000	0.000
C4H8O3	2	496.000	5.200	0.000	0.000	1.000
iC3H7	2	303.400	4.810	0.000	0.000	1.000
tC4H9	2	352.000	5.240	0.000	0.000	1.000
iC4H9	2	352.000	5.240	0.000	0.000	1.000
iC4H8	2	344.5	5.089	0.5	0.0	1.0
C4H8O	2	444.197	5.063	0.000	0.000	0.000
iC10H22	2	517.36	7.03	0.0	19.16	1.0
a-iC10H19	2	516.76	6.87	0.0	18.65	1.0
a-iC10H20	2	515.34	6.95	0.0	18.82	1.0
a-iC10H20OOH	2	677.90	7.03	0.69	20.01	1.0
a-iC10H21	2	518.79	6.95	0.0	18.99	1.0
a-iC10H21O2	2	574.04	7.11	0.69	20.01	1.0
a-iOC10H19OOH	2	747.26	7.06	0.89	20.35	1.0
a-iOOC10H20OOH	2	740.37	7.17	1.40	21.03	1.0
b-iC10H19	2	526.03	6.89	0.0	18.65	1.0
b-iC10H20	2	524.60	6.97	0.0	18.82	1.0
b-iC10H20OOH	2	676.14	7.03	0.69	20.01	1.0
b-iC10H21	2	518.79	6.95	0.0	18.99	1.0
b-iC10H21O2	2	573.14	7.11	0.69	20.01	1.0
iC9H18	2	501.19	6.68	0.0	16.97	1.0
b-iOC10H19OOH	2	751.46	7.12	0.89	20.35	1.0
b-iOOC10H20OOH	2	738.32	7.16	1.40	21.03	1.0
c-iC10H19	2	526.29	6.90	0.0	18.65	1.0
c-iC10H20	2	524.85	6.97	0.0	18.82	1.0
c-iC10H20OOH	2	671.70	7.03	0.69	20.01	1.0
c-iC10H21	2	518.79	6.95	0.0	18.99	1.0
c-iC10H21O2	2	569.77	7.12	0.69	20.01	1.0
c-iOOC10H20OOH	2	733.50	7.17	1.40	21.03	1.0
iC6H12O	2	485.27	5.89	0.2	11.93	1.0
iC9H19	2	495.16	6.66	0.0	17.14	1.0
iC9H17	2	492.91	6.58	0.0	16.80	1.0
iC7H14O	2	509.24	6.18	0.2	13.78	1.0
iC9H17O	2	564.97	6.74	0.2	17.31	1.0
iC9H18O	2	563.27	6.81	0.2	17.48	1.0
iC3H5	2	350.56	4.83	0.0	5.70	1.0
nC3H5	2	350.56	4.83	0.0	5.70	1.0
iC4H7O	2	437.02	5.36	0.2	8.06	1.0
iC5H10O	2	461.47	5.61	0.2	10.08	1.0
iC5H9O	2	462.82	5.53	0.2	9.91	1.0
iC6H11O	2	486.70	5.82	0.2	11.76	1.0
iC7H14	2	444.44	6.08	0.0	13.27	1.0
iC7H13	2	445.63	6.01	0.0	13.10	1.0
nC8H15	2	478.92	6.32	0.0	14.95	1.0
iC8H15	2	469.20	6.30	0.0	14.95	1.0
iC3H5O	1	414.68	4.94	0.2	6.21	1.0
iC4H8O	2	437.80	5.32	0.2	8.23	1.0
C2H3HCO	1	411.91	4.93	0.2	5.87	1.0
C3H5O	2	421.71	5.01	0.2	6.21	1.0
iC7H13O	2	516.76	6.17	0.2	13.61	1.0
CH3CHCO	1	359.5	4.77	0.2	6.04	1.0
C3H6O	2	420.50	5.09	0.2	6.38	1.0
C6H10O	2	483.20	5.804	2.7	11.59	1.0
C5H10CHO	2	486.73	5.817	2.7	11.76	1.0
C3H6CHO	2	438.60	5.238	2.7	8.060	1.0
C3H5CHO	2	435.60	5.223	2.7	7.890	1.0
C2H4CHO	2	414.68	4.943	2.7	6.210	1.0

```
cyC6H9Oa            2   463.81    5.352   0.4     11.42     1.0
cyC6H9Ob            2   463.81    5.352   0.4     11.42     1.0
cyC6H9Oc            2   463.81    5.352   0.4     11.42     1.0
cyC6H9Od            2   463.81    5.352   0.4     11.42     1.0
CH2CH2OH            2   470.600   4.410   0.000   0.000     1.500
CH3CH2O             2   470.600   4.410   0.000   0.000     1.500
CH3CHOH             2   470.600   4.410   0.000   0.000     1.500
C2H3OH              2   470.600   4.410   0.000   0.000     1.500
O2C2H4OH            2   523.200   5.664   1.700   0.000     1.000
C2H4O2OH            2   523.200   5.664   1.700   0.000     1.000
CH2CH2O2H           2   523.200   5.664   1.700   0.000     1.000
cyC6H11OOH          2   567.839   5.562   0.550   12.44     1.400
cyC6H9OO            2   490.382   5.555   2.900   11.93     1.900
cyC6H8OOH           2   586.370   5.441   0.550   11.93     1.400
cyOOHC6H9OOH        2   747.995   5.536   3.080   13.29     1.800
CH2CHOO             2   428.800   4.958   2.900   0.000     1.000
!1-15: Species name
! 16-80: Molecular parameters
!        molecule index: 0 = atom, 1= linear molec.
!                        2 = nonlinear molec.
!        L-J potential well depth, e/kb (K)
!        L-J collision diameter,σ, (SI)
!        Dipole moment μ, Debye
!        Polarizability,α, SI2
!        Rotational relaxation number, Zrot at 298K
!        Comments
```

Appendix IV

Sheet 1: i) Benson Bond energy [1]

Molecule		bond	ΔH0 (kJ/mol)	S0 (J/mol/K)	Cp0(300) (J/mol/K)
C3H5CHO 					
	3	[Cd-H]	13.39	57.74	10.88
	2	[C-H]	-16.02	53,97	7.28
	1	[CO-C]	-60.25	-2.51	15.48
	1	[Cd-C]	26.65	-59.83	10.88
	1	[CO-H]	-58.16	112.13	17.57
	Net		**-83.64**	**330.95**	**91.13**

Sheet 2: ii) Mech_Statis

Vibrational Contribution
$S_{vib} = R[-ln(1-e^{-x}) + \frac{x}{e^x - 1}]$
$C_{p,vib} = R\frac{x^2 e^x}{(e^x-1)^2}$ $C_p \cong 4R + C_{p,vib}$

Species			N # of atoms	M (g/ mole)	# Freq		
Type	Name	Formula			Stretching	Deformation	
Parent	3-Butenal	C3H5CHO	11	70	10	22	
Model	1,4-Pentadiene	C5H8	13	68	12	18	
					C-H	H-C-H	C=C-H
				number	2	2	2

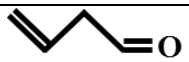
x=hvc/k_bT *dimension less freq.*	
hc/k_b =	**1.438777354**
R= *cal/mol/K*	**1.98722**
R= *J/mol/K*	**8.314**

	x(v,T) [1]							
	v							
	vibrational freq.				T			
Bond	**1/cm**	**300**	**400**	**500**	**600**	**800**	**1000**	**1500**
C=C-H Deformation	1150	5.51531319	4.136484892	3.309187914	2.757656595	2.068242446	1.654593957	1.103062638
H-C-H Deformation	1450	6.782259	5.215567908	4.172454326	3.477045272	2.607783954	2.086227163	1.390818109
C-H Stretching	3100	14.86736599	11.15052449	8.920419594	7.433682995	5.575262246	4.460209797	2.973473198
		Cp,vib(x)						
		T						
	# bond freqs	**300**	**400**	**500**	**600**	**800**	**1000**	**1500**
	2	0.245255671	0.561109301	0.856770778	1.09300036	1.408007672	1.589764986	1.797415448
	2	0.103868132	0.296815969	0.550108388	0.790435795	1.160746766	1.399836641	1.695639977
	2	0.000153426	0.003550077	0.021137012	0.064977053	0.235922601	0.467747357	0.997684882
					S,vib(x)			
		T						
		300	**400**	**500**	**600**	**800**	**1000**	**1500**
		0.052303198	0.16549136	0.323429629	0.501452841	0.86327572	1.198760121	1.890071204
		0.017551529	0.067423222	0.160680909	0.282676463	0.564435892	0.851120413	1.484451194
		1.10138E-05	0.000346925	0.002634766	0.009910538	0.049702399	0.126764802	0.42266107
						ΔS0,vib (300)		
						0.139731482	*cal/mol/K*	
						0.58463652	***J/mol/K***	

			Cp,vib(x) *Model*			
			C5H8		*calculated*	*with G.A*
			T			
300	**400**	**500**	**600**	**800**	**1000**	**1500**
23.22	29.58	35.04	39.6	46.74	52.04	60.02
			ΔCp,vib(x)		*cal/mol/K*	
			T			
300	**400**	**500**	**600**	**800**	**1000**	**1500**
0.698554457	1.722951	2.8560324	3.896826417	5.60935408	6.91469797	8.98148061
			Cp,vib(x)		*cal/mol/K*	
			C3H5CHO			
			T			
300	**400**	**500**	**600**	**800**	**1000**	**1500**
22.52144554	27.85705	32.183968	35.70317358	41.1306459	45.12530203	51.0385194
			Cp,vib(x)		***J/mol/K***	
94.22972815	116.5538943	134.65772	149.3820783	172.090623	188.8042637	213.545165

Symmetry Correction

$$\Delta S_{sym} \cong R.\ln\left(\frac{\sigma_{e,\,model}}{\sigma_{e,\,parent}}\right)$$

Species			**Structure**	**$\sigma_{e,\ ext.}$ symmetry**
Type	**Name**	**Formula**		
Parent	**3-Butenal**	**C3H5CHO/3-C4H6O**		1
Model	1,4-Pentadiene	**C5H8**		2

$\sigma_{e,\ model}$	$\sigma_{e,\ parent}$	**ΔS0, rot**	
2	1	0.686215709	*cal/mol/K*
		5.742253051	***J/mol/K***

Translational Contribution
$\Delta S_{tran} \cong 1.5\,\mathrm{R}.\ln(\frac{M_{parent}}{M_{model}})$

Species			N # of atoms	M (g/ mole)
Type	Name	Formula		
Parent	3-Butenal	C3H5CHO	11	70
Model	1,4-Pentadiene	C5H8	13	68

ΔS0, tran	
0.08640692	*cal/mol/K*
0.361526551	***J/mol/K***

ΔS0,vib (300)	+	ΔS0, Sym	+	ΔS0, tran	=	ΔS0,total (300)		+	S0,Model (300)	
0.58463652		5.742253051		0.361526551		6.688416122	*J/mol/K*		334.63632	*J/mol/K*

S0, C3H5CHO(300)	
341.3247361	***J/mol/K***

Sheet 3: iii) Joback & Reid contribution [2]

Groups	ΔP	ΔTb	ΔTc	ΔH0	ΔG0	a	b	c	d
	Non-ring (linear)								
>CH_	0.002	21.74	0.0164	29.89	58.36	-2.30E+01	2.04E-01	-2.65E-04	1.20E-07
_CH3	-0.0012	23.58	0.0141	-76.45	-43.96	1.95E+01	-8.08E-03	1.53E-04	-9.67E-08
>CH2	0	22.88	0.0189	-20.64	8.42	-9.09E-01	9.50E-02	-5.44E-05	1.19E-08
#C<	0.0011	24.14	0.0117	83.99	92.36	-2.81E+01	2.08E-01	-3.06E-04	1.46E-07
#CH2	-0.0028	18.18	0.0113	-9.63	3.77	2.36E+01	-3.81E-02	1.72E-04	-1.03E-07
#C#	0.0028	26.15	0.0026	142.14	136.7	2.74E+01	-5.57E-02	1.01E-04	-5.02E-08
#CH_	-0.0006	24.96	0.0129	37.97	48.53	-8.00E+00	1.05E-01	-9.63E-05	3.56E-08
OH alcohol	0.0112	92.88	0.0741	-208.04	-189.2	2.57E+01	-6.91E-02	1.77E-04	-9.88E-08
OH phen.	0.0184	76.34	0.024	-221.65	-197.37	-2.81E+00	1.11E-01	-1.16E-04	4.94E-08
_O_	0.0015	22.42	0.0168	-132.22	-105	2.55E+01	-6.32E-02	1.11E-04	-5.48E-08
>C#O	0.0031	76.75	0.038	-133.22	-120.5	6.45E+00	6.70E-02	-3.57E-05	2.86E-09
O#CH_	0.003	72.24	0.0379	-162.03	-143.48	3.09E+01	-3.36E-02	1.60E-04	-9.88E-08
_COOH	0.0077	169.09	0.0791	-426.72	-387.87	2.41E+01	4.27E-02	8.04E-05	-6.87E-08
#O	0.0101	-10.5	0.0143	-247.61	-250.83	6.82E+00	1.96E-02	1.27E-05	-1.78E-08
COO	0.0005	81.1	0.0481	-337.92	-301.95	2.45E+01	4.02E-02	4.02E-05	-4.52E-08
>C<	0.0043	18.25	0.0067	82.23	116.02	-6.62E+01	4.27E-01	-6.41E-04	3.01E-07

						Cp			
Molecule	**Groups**	**ΔH0**	300	400	500	600	800	1000	1500
C3H5CHO/ 3-C4H6O	(#CH2)(#CH-)(>CH2)(O#CH-)	-20.5542284	21.9001194	26.932107	31.2586001	34.9537028	40.7461538	44.9022934	52.0242475
	J/mol/K	**-86.00**	**91.63**	**112.68**	**130.79**	**146.25**	**170.48**	**187.87**	**217.67**

$$C_p = \sum(a) - 39.73 + \left[\sum(b) + 0.21\right]T + \left[\sum(c) - 3.91e-4\right]T^2 + \left[\sum(d) + 2.06e-7\right]T^3$$

$$\Delta H^0_{f,298} = 68.29 + \sum \Delta H$$

Sheet 4: iv) Sheet4 C-(C_d)(CO)(H_2)

Benson, Bond energy(ΔHf0,S0,Cp0)

Molecule	Groups	ΔH0	S0	Cp0(300)
C3H5CHO/3-C4H6O		-83.64	330.95	91.13
-1	Cd-(H)2	26.19	115.52	21.34
-1	Cd-(C)(H)	35.94	33.35	17.41
-1	CO-(C)(H)	-121.75	146.02	29.29
	C-(Cd)(CO)(H)2	-24.02	36.07	23.10

Benson, Struct.(trans,rot,vib) & Bond energy(ΔHf0)

							Cp			
Molecule	Groups	ΔH0	S0	300	400	500	600	800	1000	1500
C3H5CHO/3-C4H6O		--	341.32	94.23	116.55	134.66	149.38	172.09	188.80	213.55
-1	Cd-(H)2	--	115.52	21.34	26.61	31.42	35.56	42.13	47.15	55.19
-1	Cd-(C)(H)	--	33.35	17.41	21.05	24.31	27.20	32.01	35.35	40.25
-1	CO-(C)(H)	--	146.02	29.29	32.64	36.82	40.58	46.86	51.04	56.07
	C-(Cd)(CO)(H)2	--	46.43	26.20	36.26	42.11	46.04	51.09	55.25	62.04

Joback & Reid

						Cp			
Molecule	Groups	ΔH0	300	400	500	600	800	1000	1500
C3H5CHO/3-C4H6O		-86.00	91.63	112.68	130.79	146.25	170.48	187.87	217.67
-1	Cd-(H)2	26.19	21.34	26.61	31.42	35.56	42.13	47.15	55.19
-1	Cd-(C)(H)	35.94	17.41	21.05	24.31	27.20	32.01	35.35	40.25
-1	CO-(C)(H)	-121.75	29.29	32.64	36.82	40.58	46.86	51.04	56.07
	C-(Cd)(CO)(H)2	-26.38	23.60	32.39	38.24	42.90	49.48	54.32	66.17

Sheet 5: v) Sheet5 Summary

			C_p(T,°K)						
Method	$\Delta_f H^0$	S^0	300°	400°	500°	600°	800°	1000°	1500°
Additivity of Bond Properties, Statistical Mechanics Estimation & Group Contribution Methods									
i) Benson Bond energy									
ii) Statistc. Mech.									
iii) Joback & Reid									

C-(Cd)(CO)(H)2			C_p(T,°K) (cal·mol-1·K-1)						
Method	$\Delta_f H^0$	S^0	300°	400°	500°	600°	800°	1000°	1500°
2.2) Additivity of Bond Properties, Statistical Mechanics Estimation & Group Contribution Methods									
i) Benson Bond energy	-24.02	36.07	23.10	-	-	-	-	-	-
ii) Statistc. Mech.	-	46.43	26.20	36.26	42.11	46.04	51.09	55.25	62.04
iii) Joback&Reid	-26.38		23.60	32.39	38.24	42.90	49.48	54.32	66.17
mean value	**-25.20**	**41.25**	**24.30**	**34.33**	**40.17**	**44.47**	**50.28**	**54.78**	**64.10**
Standard deviation	1.2	7.3	1.4	1.9	1.9	1.6	0.8	0.5	2.1

References:

[1]: S. W. Benson, Thermochemical Kinetics, New York, USA: John Wiley & Sons Ltd., 2nd Edition, 1976.

[2]: Joback, K. G., Reid. R. C., "Estimation of Pure-Component Properties from Group-Contributions," Chem. Eng. Comm. 1987, vol. 57, pp. 233-243.

Appendix V

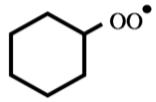
Table A.1. Benson's groups. symmetry numbers and NASA-coefficients for selected species.

Structure	groups	No.
	$C-(C)_2(H)_2$	3
	$C-(C•)(C)(H)_2$	2
	$C•-(C)_2(H)$	1
	RC10	6

NASA Coefficients

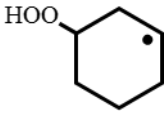
Species	a_1	a_2	a_3	a_4	a_5
cyC_6H_{11}	0.57261502E+01	0.49173558E-01	-0.23796767E-04	0.54208507E-08	-0.47445368E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	0.10056946E+04	-0.11973133E+02	-0.10741222E+01	0.34294293E-01	0.64592225E-04
Sym. numbers*	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(2/1)	-0.10261825E-06	0.40853054E-10	0.45268762E+04	0.31367410E+02	0.61161896E+04

*(external/ internal)

Structure	groups	No.
	O-(C)(O•)	1
	$C-(C)_2(H)_2$	5
	$C-(C)_2(O)(H)$	1
	RC10	6

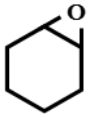
NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
$cyC_6H_{11}OO·$	-0.20839567E+00	0.68532755E-01	-0.35407414E-04	0.85310323E-08	-0.78298305E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	-0.13493035E+05	0.24862162E+02	0.76560000E+00	0.29242014E-01	0.99097744E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(2/1)	-0.14795512E-06	0.59505351E-10	-0.12592840E+05	0.27262169E+02	-0.10455858E+05

Structure	groups	No.
	O-(O)(C)	1
	O-(O)(H)	1
	$C-(C)_2(H)_2$	2
	$C-(C•)(C)(H)_2$	2
	$C-(C)_2(O)(H)$	1
	$C•-(C)_2(H)$	1
	RC10	6

NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
$cyC_6H_{10}OOH$	0.91017065E+01	0.52091518E-01	-0.25944131E-04	0.60871367E-08	-0.54676862E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	-0.89772135E+04	-0.22534805E+02	-0.17750211E+01	0.71010961E-01	-0.22421128E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(1/1)	-0.11354775E-07	0.53233922E-11	-0.55480956E+04	0.36264454E+02	-0.31416887E+04

Structure	groups	No.
	$O-(C)_2$	1
	$C-(C)_2(O)(H)$	2
	$C-(C)_2(H)_2$	4
	RC10	4
	RC1	1

NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
a-$cyC_6H_{10}O$	-0.80846809E+01	0.78416058E-01	-0.42966125E-04	0.10802297E-07	-0.10236452E-11
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	-0.15124674E+05	0.60499401E+02	-0.16543292E+01	0.42696025E-01	0.62179263E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(2/1)	-0.11687253E-06	0.50777343E-10	-0.17184963E+05	0.28835473E+02	-0.15440221E+05

Structure	groups	No.
	O-(C)$_2$	1
	C-(C)$_2$(O)(H)	2
	C-(C)$_2$(H)$_2$	4
	RC10	3
	RC2	1

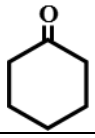
NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
b-cy$C_6H_{10}O$	-0.94946020E+01	0.80553090E-01	-0.44208480E-04	0.11132126E-07	-0.10563421E-11
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	-0.15606945E+05	0.65125482E+02	0.29262009E+01	0.65415817E-02	0.15371109E-03
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(2/1)	-0.21344824E-06	0.87175623E-10	-0.18496486E+05	0.71794684E+01	-0.16357950E+05

Structure	groups	No.
	O-(C)$_2$	1
	C-(C)$_2$(O)(H)	2
	C-(C)$_2$(H)$_2$	4
	RC10	2
	RC3	1

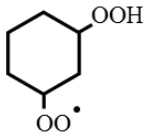
NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
c-cy$C_6H_{10}O$	-0.95853077E+01	0.80577563E-01	-0.44174188E-04	0.11116295E-07	-0.10544255E-11
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	-0.25530791E+05	0.61862506E+02	0.16169856E+01	0.11188534E-01	0.14771115E-03
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(4/1)	-0.21071414E-06	0.87058128E-10	-0.28165251E+05	0.98415047E+01	-0.26258119E+05

Structure	groups	No.
	CO-(C)$_2$	1
	C-(CO)(C)(H)$_2$	2
	C-(C)$_2$(H)$_2$	3
	RC10	6

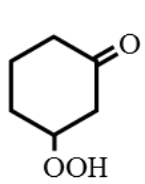
NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
d-cy$C_6H_{10}O$	-0.66687497E+00	0.60687596E-01	-0.30099302E-04	0.70125266E-08	-0.62731530E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	-0.31167893E+05	0.26362479E+02	-0.78489570E+01	0.93504999E-01	-0.94472350E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(2/1)	0.71093411E-07	-0.25979669E-10	-0.29886581E+05	0.60321458E+02	-0.28779168E+05

Structure	groups	No.
	O-(C)(O•)	1
	O-(O)(C)	1
	O-(O)(H)	1
	C-(C)$_2$(O)(H)	2
	C-(C)$_2$(H)$_2$	4
	RC10	6

NASA Coefficients

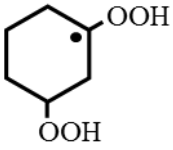
Species	a_1	a_2	a_3	a_4	a_5
cy·$OOC_6H_{10}OOH$	0.20094503E+01	0.74073855E-01	-0.39254193E-04	0.96576588E-08	-0.90066937E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	-0.25674718E+05	0.20565845E+02	-0.17398958E+01	0.71686526E-01	0.72801188E-05
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(1/1)	-0.58960561E-07	0.27307535E-10	-0.24730231E+05	0.41406273E+02	-0.22104883E+05

Structure	groups	No.
	O-(O)(C)	1
	O-(O)(H)	1
	C-(C)$_2$(O)(H)	1
	C-(C)$_2$(H)$_2$	2
	C-(CO)(C)(H)$_2$	2
	CO-(C)$_2$	1
	RC10	6

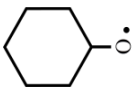
NASA Coefficients					
Species	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**
cyOC$_6$H$_9$OOH	0.31662570E+00	0.69003372E-01	-0.36037339E-04	0.87559801E-08	-0.80895897E-12
linearity	**a_6**	**a_7**	**a_8**	**a_9**	**a_{10}**
	-0.42944421E+05	0.28684832E+02	-0.83287424E+01	0.12266269E+00	-0.15487972E-03
Sym. numbers	**a_{13}**	**a_{12}**	**a_{13}**	**a_{14}**	**a_{15}**
(1/1)	0.12834888E-06	-0.46584898E-10	-0.42257621E+05	0.65746476E+02	-0.40428193E+05

Structure	groups	No.
	C$_d$-(C)(H)	2
	C-(C$_d$)(C)(H)$_2$	2
	C-(C)$_2$(H)$_2$	2
	RC9	1

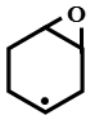
NASA Coefficients					
Species	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**
cyC$_6$H$_{10}$	0.39442769E+01	0.47473657E-01	-0.23199637E-04	0.53766657E-08	-0.47931014E-12
linearity	**a_6**	**a_7**	**a_8**	**a_9**	**a_{10}**
non-linear	-0.44509693E+04	-0.29390438E+00	-0.27517028E+01	0.48912768E-01	0.19511676E-04
Sym. numbers	**a_{13}**	**a_{12}**	**a_{13}**	**a_{14}**	**a_{15}**
(2/1)	-0.59644226E-07	0.27082294E-10	-0.19687471E+04	0.37948748E+02	-0.54967525E+03

Structure	groups	No.
	O-(O)(C)	1
	O-(C•)(O)	1
	O-(O)(H)	2
	C•-(C)$_2$(O)	1
	C-(C•)(C)(H)$_2$	2
	C-(C)$_2$(H)$_2$	2
	C-(C)$_2$(O)(H)	1
	RC10	6

NASA Coefficients					
Species	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**
cyC6H9(OOH)$_2$	0.13296721E+02	0.56179584E-01	-0.28298589E-04	0.66759657E-08	-0.60158400E-12
linearity	**a_6**	**a_7**	**a_8**	**a_9**	**a_{10}**
non-linear	-0.21992272E+05	-0.40186252E+02	-0.55936490E+01	0.12238953E+00	-0.13187643E-03
Sym. numbers	**a_{13}**	**a_{12}**	**a_{13}**	**a_{14}**	**a_{15}**
(1/1)	0.97940639E-07	-0.35615990E-10	-0.17494214E+05	0.54214822E+02	-0.14713736E+05

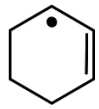
Structure	groups	No.
	C-(O•)(C)$_2$(H)	1
	C-(C)$_2$(H)$_2$	5
	RC10	6

NASA Coefficients					
Species	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**
cyC$_6$H$_{11}$O	0.32637255E+01	0.58784029E-01	-0.29394748E-04	0.68775840E-08	-0.61578610E-12
linearity	**a_6**	**a_7**	**a_8**	**a_9**	**a_{10}**
non-linear	-0.12963675E+05	0.23642621E+01	-0.38078981E+01	0.57665454E-01	0.17189370E-04
Sym. numbers	**a_{13}**	**a_{12}**	**a_{13}**	**a_{14}**	**a_{15}**
(2/1)	-0.53677606E-07	0.21536939E-10	-0.10152550E+05	0.43686705E+02	-0.86709165E+04

Structure	groups	No.
	C-(C)$_2$(O)(H)	2
	C•-(C)$_2$(H)	1
	C-(C•)(C)(H)$_2$	2
	C-(C)$_2$(H)$_2$	1
	O-(C)$_2$	1
	RC10	4
	RC1	1

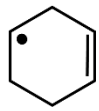
NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
a-cyC$_6$H$_9$O	-0.74704407E+01	0.74757622E-01	-0.41387678E-04	0.10473466E-07	-0.99677029E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	0.60398853E+04	0.59505359E+02	-0.23187144E+01	0.50151874E-01	0.34652255E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(1/1)	-0.86353641E-07	0.39225621E-10	0.40066875E+04	0.32724381E+02	0.56964157E+04

Structure	groups	No.
	C•-(H)(C)(C$_d$)	1
	C$_d$-(C•)(H)	1
	C$_d$-(C)(H)	1
	C-(C$_d$)(C)(H)$_2$	1
	C-(C•)(C)(H)$_2$	1
	C-(C)$_2$(H)$_2$	1
	RC7	1

NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
1,3-cyC$_6$H$_9$	0.48230902E+01	0.43906891E-01	-0.21524326E-04	0.49885999E-08	-0.44431982E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	0.10570260E+05	-0.50750458E+01	-0.43595073E+01	0.60597409E-01	-0.13999007E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(1/1)	-0.24483785E-07	0.13990165E-10	0.13380358E+05	0.44118420E+02	0.14606688E+05

Structure	groups	No.
	C•-(C)$_2$(H)	1
	C-(C•)(C)(H)$_2$	1
	C$_d$-(C)(H)	2
	C-(C$_d$)(C)(H)$_2$	1
	C-(C•)(C$_d$)(H)$_2$	1
	RC7	1

NASA Coefficients

Species	a_1	a_2	a_3	a_4	a_5
1,4-cyC$_6$H$_9$	0.39653625E+01	0.44688860E-01	-0.22101693E-04	0.51691476E-08	-0.46400342E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	0.18469954E+05	0.15519697E+01	0.11513849E+01	0.24349750E-01	0.68252173E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(1/1)	-0.10615713E-06	0.43656116E-10	0.20343077E+05	0.22231144E+02	0.22180659E+05

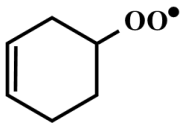
Structure	groups	No.
	C$_d$-(C)(H)	4
	C-(C$_d$)$_{2(}$(H)$_2$	2
	RC9	1

NASA Coefficients

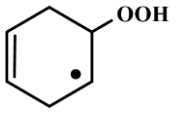
Species	a_1	a_2	a_3	a_4	a_5
1,4-cyC$_6$H$_8$	0.60072048E+01	0.38131392E-01	-0.18750123E-04	0.43570611E-08	-0.38863868E-12
linearity	a_6	a_7	a_8	a_9	a_{10}
non-linear	0.88163073E+04	-0.18395532E+02	0.19112107E+01	0.14754449E-01	0.91475839E-04
Sym. numbers	a_{13}	a_{12}	a_{13}	a_{14}	a_{15}
(3/1)	-0.13476207E-06	0.55972633E-10	0.11366314E+05	0.10445281E+02	0.13158528E+05

Structure	groups	No.
	C_d-(C)(H)	2
	C-(C_d)(C)$(H)_2$	2
	C_d-(C_d)(H)	2
	RC8	1

NASA Coefficients					
Species	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**
1,3-cyC_6H_8	0.57911078E+01	0.38887445E-01	-0.19353118E-04	0.45417154E-08	-0.40833894E-12
linearity	**a_6**	**a_7**	**a_8**	**a_9**	**a_{10}**
non-linear	0.85461589E+04	-0.95072842E+01	0.17881209E+01	0.14442450E-01	0.95904952E-04
Sym. numbers	**a_{13}**	**a_{12}**	**a_{13}**	**a_{14}**	**a_{15}**
(2/1)	-0.14190881E-06	0.59226641E-10	0.11037921E+05	0.18868425E+02	0.12806110E+05

Structure	groups	No.
	O-(C)(O•)	1
	C_d-(C)(H)	2
	C-(C_d)(C)$(H)_2$	2
	C-$(C)_2$$(H)_2$	1
	C-$(C)_2$(O)(H)	1
	RC7	1

NASA Coefficients					
Species	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**
cyC_6H_9OO	-0.15752926E+01	0.63566897E-01	-0.33475432E-04	0.82122290E-08	-0.76530877E-12
linearity	**a_6**	**a_7**	**a_8**	**a_9**	**a_{10}**
non-linear	0.22864969E+04	0.36636285E+02	-0.16012226E+01	0.51507380E-01	0.25977280E-04
Sym. numbers	**a_{13}**	**a_{12}**	**a_{13}**	**a_{14}**	**a_{15}**
(1/1)	-0.73889337E-07	0.33956656E-10	0.21056130E+04	0.37835261E+02	0.40149146E+04

Structure	groups	No.
	O-(O)(C)	1
	O-(O)(H)	1
	C_d-(C)(H)	2
	C-(C_d)(C)$(H)_2$	1
	C-(C•)(C_d)$(H)_2$	1
	C-(C•)(C)(O)(H)	1
	C•-$(C)_2$(H)	1
	RC7	1

NASA Coefficients					
Species	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**
cyC_6H_8OOH	0.65407841E+01	0.49378665E-01	-0.25554660E-04	0.62086740E-08	-0.57419865E-12
linearity	**a_6**	**a_7**	**a_8**	**a_9**	**a_{10}**
non-linear	0.87506338E+04	-0.54098324E+01	0.47690303E+00	0.60864654E-01	-0.18222490E-04
Sym. numbers	**a_{13}**	**a_{12}**	**a_{13}**	**a_{14}**	**a_{15}**
(1/1)	-0.15492520E-07	0.83620658E-11	0.10265509E+05	0.26325566E+02	0.12922781E+05